INVESTIGATING THE EMISSIONS OF NANOMATERIALS FROM COMPOSITES AND OTHER SOLID ARTICLES DURING MACHINING PROCESSES



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Investigating the Emissions of Nanomaterials from Composites and Other Solid Articles during Machining Processes

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EXECUTIVE SUMMARY

The benefits of more durable and tough composite materials that contain nano-objects are promoting the emergence of a new range of advanced, modern consumer products. Nano-objects in various forms are used to obtain these benefits, but are there safety issues associated with their use in composites?

This report examines particle release from the machining of composite materials that contain nano-objects in a number of shapes and forms. It summarises the type of nano-composite materials investigated, the machining processes that were used to shape the materials, how particle release was measured and characterised, what precautions were taken to control particle release in the work environment and what are the levels of releases. The last chapter identifies outstanding issues.

The machining of a number of composite forms has been examined by investigators. Matrices include epoxy, polycarbonate, polyurethane, polymethyl methacrylates and polyamide. Nano-objects used for reinforcing include silica, carbon fibres, carbon nanotubes and nanoclay. Machining processes investigated include wet and dry cutting, drilling, grinding, sanding and abrasion.

Measurement techniques are available that can detect and measure emissions, though there is some uncertainty regarding the capability of detecting small quantities of free nano-objects emitted during machining.

A summary of the findings from the review of experimental work is:

- The overall mass of emissions from the machining of composites containing reinforcing nano-objects is in most instances not significantly different from the machining of composites not containing nano-objects.
- High energy processes emit significantly higher numbers of particles and produce higher airborne mass concentrations than low energy processes.
- For some processes, lower emissions can be achieved by using wet machining in place of dry machining.
- Currently there is insufficient data to arrive at any conclusions about how emissions vary with material composition.
- A combination of; (a) nanoscale particles nanoparticles from the matrix primarily but also free reinforcing nano-objects, (b) agglomerates or aggregates of nanoobjects, and (c) matrix with nano-objects embedded are emitted. The machining of composites can result in nano-objects that are partially embedded in matrix fragments.
- Only one incidence of free individual carbon nanotubes (CNT) being detected has been reported (in the release from an abrasion experiment), while a number of studies examining the machining of CNT-containing composites did not find such a release. Free carbon nanofibres have also been detected in a machining study.

• As for emissions control generally, use of engineering controls with machining equipment can be used to significantly reduce worker exposure, if designed appropriately and maintained adequately.

Thus, while taking into consideration that machining processes such as high energy cutting are of short duration (typically less than one minute per task), it is concluded that high energy machining of composites containing reinforcing nano-objects can present a health risk because of the quantities of material emitted and also, submicrometre particles can remain suspended in the air for very long times. The use of engineering controls to minimise exposure is recommended.

Lower energy machining processes generally emit significantly lower levels of material. By examining the particle control values, these levels of emissions should not present a significant health risk if low toxicity particles are emitted, but can be significant if emitted particles are biopersistent fibres or otherwise have high toxicity.

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Glossary

APS	Aerodynamic Particle Sizer
AS	Aerosol Spectrometer
AUC	Analytical Ultra-Centrifugation
BEL	Benchmark Exposure Level
BZ	Breathing Zone
Buckypaper	A sheet of Carbon Nanotubes, formed in a paper-making process
СВ	Carbon Black
CF	Carbon Fibre (not nanoscale)
CNC	Computer Numerical Controlled
CNF	Carbon Nanofibres (nanoscale)
CNT	Carbon Nanotubes (nanoscale)
CPC	Condensation Particle Counter
CVD	Chemical Vapour Deposition
DC	Diffusion Charger
DiSC	Diffusion Size Classifier
DMA	Differential Mobility Analyser
DPM	Diesel Particulate Matter Analyser (see EC, OC)
EC	Elemental Carbon (e.g. Fullerenes, CNT)
EDM	Electrical Discharge Machining
EDX	Energy Dispersive X-ray Spectroscopy (also EDS or EDXS)
EEPS	Engine Exhaust Particle Sizer
EL	Exposure Limit
ELPI	Electrostatic Low-Pressure Impactor
ENM	Engineered Nanomaterial
ESP	Electrostatic Precipitator
FAS	Particle Analysis System (suspensions)
FIB	Focused Ion Beam (nano-scale milling)
FMPS	Fast Mobility Particle Sizer
FRP	Fibre-Reinforced Plastics
FSW	Friction Stir Welding

HARN	High Aspect Ratio Nano-object
HSS	High-Speed Steel
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ISO	International Organization for Standardization
LAP	Laser Aerosol Particle size spectrometer
LEV	Local Exhaust Ventilation
MCE	Mixed Cellulose Ester (membrane material)
micro-EDM	Electrical Discharge micro-Machining
MMAD	Mass Median Aerodynamic Diameter
MPPS	Most Penetrable Particle Size
MWCNT	Multi-Walled CNT
Nano-ID Select	See PWRAS
NAS	Nanometer Aerosol Sampler (electrostatic)
NEAT	Nanoparticle Emission Assessment Technique (NIOSH)
NM	Nanomaterial
NP	Nanoparticle
NSAM	Nanoparticle Surface Area Monitor (AeroTrak 9000, 3550)
OC	Organic Carbon: general organic chemical compounds that are not Elemental Carbon (EC)
OPC	Optical Particle Counter
OPC-RPM	Optical Particle Counter in a mode that measures Respirable Particulate Matter, rather than number count.
OPS	Optical Particle Sizer
PA	Polyamide
РАН	Polycyclic Aromatic Hydrocarbons
PAS	Photoelectric Aerosol Sensor
PCM	Phase-Contrast Microscopy
PECVD	Plasma Enhanced Chemical Vapour Deposition
PEL	Permissible Exposure Limit (enforced by OSHA)
PMMA	Polymethyl methacrylates
POM	Polyoxymethylene
PPE	Personal Protective Equipment
PSD	Particle Size Distribution
PU	Polyurethane

PVA	Polyvinyl acetate
PVC	Polyvinyl chloride
PVD	Physical Vapour Deposition
PWRAS	Portable Wide-Range Aerosol Sampler (Naneum)
REL	Recommended Exposure Limits (NIOSH)
RER	Room Exchange Rate (in Ventilation)
RPM	Rotations per Minute
SEM	Scanning Electron Microscopy
SIMS	Secondary-Ion Mass Spectroscopy
SMPS	Scanning Mobility Particle Sizer
STEL	Short Term Exposure Limit (15 minute TWA)
Swarf	Any fine waste produced by a machining operation, especially when in the form of strips or ribbons.
SWCNT	Single-Walled CNT
Taber Abraser	A proprietary type of abrasion test instrument
ТЕМ	Transmission Electron Microscopy
TLV	Threshold Limit Values
ТР	Thermophoretic Precipitator
TPNC	Total Particle Number Concentration
TPU	Thermoplastic PolyUrethane
TWA	Time Weighted Average (generally over 8 hour period)
UNPA	Universal Nano Particle Analyser (DMA + NSAM)
UV	Ultra-Violet light
VOC	Volatile Organic Compounds
WC	Tungsten Carbide
WEL	Workplace Exposure Limit
WES	Workplace Exposure Standard
WRAS	Wide Range Aerosol Spectrometer (Grimm)
XPS	X-ray Photoelectron Spectroscopy
Ø	Diameter (particle, fibre)

1. INTRODUCTION

Safe Work Australia commissioned CSIRO to undertake a review to:

- Determine current methods that are used to assess and measure releases of manufactured nanomaterials (including carbon nanotubes) during the cutting or machining of composite materials or other articles.
- Determine which composites or other articles, which nanomaterials within composites or other articles and which cutting or machining activities may give rise to exposure scenarios as a result of machining.
- Determine levels of emissions or exposures during machining or cutting of nanomaterial-containing articles or composites and relate to the workplace controls used in each case if the information is provided.
- Determine key issues and/or knowledge gaps which require further examination, for example through experimental research.

The approach is to first develop criteria and select relevant literature, as done in Section 1.1, from which information is extracted and collated on specific focus areas of interest. These areas include the type of materials and articles described in the selected literature (Section 2), the type of release and exposure that may result from the manufacturing, use and disposal of such articles (Section 3), how the release of nano-objects is currently being measured (Section 4), data from measured emissions (Section 5), assessment of emissions (Section 6) and what gaps in current knowledge have been identified (Section 7).

1.1 Literature Selection

Considering the large number of publications that are available on the subject of advanced nanomaterials and composites, it was necessary to devise a concept for the selection of literature for the review. This investigation is focusing on published literature in the context of the following four key criteria:

- 1. Machining for product manufacture
- 2. Composite materials
- 3. Materials containing nano-structured objects
- 4. Measurement of particle release during processing

Results obtained from topic searches were compared to information provided by more general review articles [1-3], which were addressing various fields of interest to this report. Only 17 publications were found at this point in time that are covering all four criteria, but there are more that cover three criteria out of the whole set of four and are useful to be considered because they are adding new viewpoints to the task at hand. All these publications are summarised in Table 1.

	Machining	Composite	Nano- objects	Particle Release	References
Assess Risk in Advanced Composite Manufacturing	✓	✓	*	✓	[4-20]
Advanced Composite Precursors	×	✓	✓	√	[21-26]
Nanoparticle and Precursor Manufacture	×	×	√	×	[27-29]
High Performance Tooling	✓	✓	×	✓	[30-34]
Advanced Novel Machining Techniques	✓	✓	✓	×	[35-41]

Table 1: Selected literature grouped according to the key criteria (shown across the top) they fulfil.

In carrying out this selection it is necessary to clarify the lines drawn in what satisfies a criterion and what does not.

The term "machining" implies that the shape of a workpiece is changed by means of a mechanical tool. The purpose of the machining also needs to be considered, distinguishing if the process is used for manufacturing of an article or for simulating reproducible conditions to extract some kind of universal and comparable characteristics.

Composite materials are engineered from two or more constituent materials with significantly different physical or chemical properties, which remain separate and distinct at the macroscopic or microscopic scale within the finished structure [42]. We will include in this definition ceramic materials such as cemented carbide because of the distinct microscopic separation of tungsten and cobalt phases in the alloy. These materials are of significance for high performance tools that are used for the machining of extra abrasive and tough materials, such as nano-composites.

The term "nano-object" is used according to ISO Standard ISO/TS 27687 [43] to describe a material with at least one dimension in the nanoscale, i.e. within a range of approximately 1nm to 100nm. A "nanoparticle" is defined to have all three dimensions in the nanoscale, while a "nanofibre" has two similar dimensions in the nanoscale and the third dimension significantly larger. We will adopt this definition for the purpose of this report while keeping in mind that emission of larger particles must be considered,

as was outlined in a report compiled by Queensland University of Technology and Workplace Health and Safety Queensland, commissioned by Safe Work Australia [22].

In assessing the "release" of particles and nano-objects from machining processes it is necessary to consider that particle emissions will include those generated by the workpiece as well as those from the machining tool during the machining process.

Some of the studies were concerned with materials for which it was difficult to decide if they fulfilled criteria such as "nano" or "composite". These references were still included in the selection provided that there was a clear relevance to industrial applications [30, 31, 41].

2. TYPES OF COMPOSITES AND ARTICLES CONTAINING NANOMATERIALS FOR WHICH THE MACHINING PROCESS HAS BEEN INVESTIGATED

Information on the role of novel composite materials in research and the development of consumer products is typically fairly general in nature [8, 44, 45], but a description of performance properties is often available at various levels of detail. For instance, achievable performances and resulting design considerations have been investigated by Kumar *et al.* [46].

Reports of machining investigations conducted on novel advanced composites, other composites and coatings that contain nano-materials of any form are listed in Table 2. Materials investigated in these references are often highly relevant to various markets as some of these studies have been conducted by companies themselves, while research laboratories generally used commercial precursors to conduct these investigations for the purpose of assessing the safety of potential products.

In terms of materials that have been investigated as machining work pieces we find that the vast majority are polymeric composite sheets and coatings. The only inorganic matrix material is a metal-oxide powder used in conjunction with lithium-titanate (Li-Ti-MO, [27]) that has been noted for its superior performance in fuel cells. There is however a wide range of nanostructured metal oxides available (ZnO, TiO₂, Al₂O₃, and Fe₂O₃) that are widely used as a nano-additive for various composites. The most prominent additives, however, are carbon nanotubes (CNT). Other additives include nano-structured silicon and nano-clays.

Nano-composite	Nano-objects	Study
Epoxy coated CNF	CNF	[7]
CNF composite	CNF	[7, 19]
Epoxy-CNF / CNF Buckypaper Laminate	CNF	[19]
Polyamide + SiO ₂ NP	SiO ₂ nanofiller, Aerosil R8200	[15]
Polyamide + Nanoclay	Clay nanofiller	[9]
PMMA + Cu NP	Copper NP	[17]
PMMA, CNT-enforced	CNT	[37, 38] [39]
Epoxy, CNT-enforced	CNT (Baytubes)	[18] [14]
Polycarbonate, CNT-enforced	CNT	[17]
POM + CNT	CNT (Nanocyl NC7000)	[15]

Table 2: Summary of composite materials and coatings containing nano-objects that have been the subject of machining studies.

Nano-composite	Nano-objects	Study
Thermoplastic PU + CNT	CNT (Nanocyl NC7000)	[20]
[Carbon fibre + CNT] epoxy composites	CNT	[4]
Laminate of base alumina fibres with CNT grown on fibres and epoxy matrix	CNT	[5, 6]
Cement mortar + CNT	CNT	[15]
Cement mortar + Calcium silicate hydrate (CSH)	CSH nano-filler (seed NP)	[15]
Concrete + fumed silica (Emaco Nano-Crete R4, BASF)	Fumed silica (Evonik)	[8]
Architectural coating (BASF Acronal LR 8976) + ZnO NP	ZnO NP susp: NANOBYK-3820	[12]
Architectural coating (BASF Acronal LR 8976) + Fe ₂ O ₃ NP	Fe ₂ O ₃ NP	[13]
Polyurethane (PU) coating (2 component) + ZnO NP	ZnO NP: LP-X 21217	[12] [13]
Clearcoat, Desmolux U100 + ZnO NP	ZnO NP: LP-X20878	[12]
UV Hardcoat + SiO ₂ sol	Nano-SiO ₂ sol	[11]
Acryl paint + TiO₂ (anatase) Acryl paint + CB	• TiO₂: UV Titan • Flammrüss 101	[11]
Outdoor acryl paint + SiO ₂ sol	Nano-SiO ₂ sol	[11]
PVA paint + TiO ₂ (anatase)	TiO ₂ : W2730	[10, 11]
PET fabric, PVC coated + Nano-clay	Nano-clay: IFTH, Lyon	[16]
Thermally sprayed nano-powders (coatings)	• WC / 12Co • Al ₂ O ₃ / 13TiO ₂	[40]
Cermet: Si ₃ N ₄ + TiN + Si ₃ N _{4w}	TiN NP; Si ₃ N ₄ nano whiskers	[35]
Cermet: Cemented carbide	WC / Co: ISO K10	[36]
Bismaleimide + Graphite (aerospace industry)	WC in cement. carbide	[41]

3. DISCUSSION OF POTENTIAL EXPOSURE SCENARIOS

This section covers the main processes of particle generation and modification that are of significant importance to potentially exposing people to nano-objects, which includes, more recently, nano-fibres in addition to the more common nanoparticles.

The nature of particle agglomeration is revisited briefly as well as recent techniques that allow forces involved in agglomeration to be quantified (Section 3.1). A wide range of nano-composite sources are investigated in Section 3.2 for the release of particles and nano-objects during the process of machining.

3.1 Particle Adhesion and Agglomeration

Jordan noted in 1954 that small particles have by nature a tendency to adhere to each other as well as to solid surfaces [47]. This tendency increases in strength as the particles become smaller. Hwang et al. have investigated ways of removing particles from semiconductor surfaces [48]. Their account describes how this task becomes more difficult as particle size decreases from 50nm to 20nm and finally 10nm. For the latter, the adhesion becomes so strong that complete particle removal was not achieved even under severe bombardment by Argon "bullets" in Helium at pressures up to 30,000 Torr (4 MPa).

For composite materials, it is necessary to consider the nature of adhesion forces at the interface between the matrix material and the nanoparticle. Such measurements have been performed for carbon nanotubes (CNT) in a polymeric matrix by measuring the force required to pull out a single CNT using an AFM cantilever [49, 50]. The measured interfacial shear strength varies between several MPa and several 100's of MPa, depending on the matrix material used. It is comparable to the tensile strength of a polyester filament but significantly lower than the strength measured for individual CNT, which is greater than 10,000 MPa. For a CNT embedded in a solid matrix, it is therefore more likely that the CNT will be pulled out of the matrix under the application of force and less likely that it will break.

3.2 Sources of Particle Release

Novel materials with a composite structure are making an increasingly large impact on engineering in the development of products for use in airplanes [44] and in highly sophisticated tooling for enormously tough and abrasion-resistant materials. The composition of such composites can be of organic (product articles) or inorganic (tools) nature and the release of airborne particles during machining can originate from the workpiece itself, the tool or from a combination of the two.

Other machining techniques involve no direct contact of a machining tool with the workpiece, as is the case for electro-physical processes such as electro-discharge machining (EDM) [51, 52] and laser machining by pulses in the ultra-violet wavelength spectrum [53] or using ultra-short light pulses of femto-second duration [54-56], where

material is removed by converting it into a plasma. These processes generate ultra-fine particles by condensation of chemical compounds in the plasma. This aspect can be used in reverse e.g. in the synthesis of single-wall carbon nanotubes (SWCNT) by laser ablation [57, 58].

3.3 Machining Processes Investigated

Machining processes investigated comprise conventional processes like grinding, sanding, sawing, milling and turning. These are summarised in Table 3 below. More unusual but increasingly important in the shaping of ultra-tough and abrasive composite materials are processes such as Electrical Discharge Machining (EDM), Friction Stir Welding (FSW) and ultra-short pulse laser cutting. Processes like Focused Ion Beam (FIB) milling are not commonly regarded as "machining" processes, but that notion may change as technology pushes on deeper into the nanoscale.

There are also processes that have been developed specifically as controlled test scenarios to mimic the effect of use (e.g. abrasion tests) or exposure (UV chambers) on consumer products.

Abrasion tests have been developed initially to determine the durability of solid materials or fabrics but are now used as test beds for assessing particle release during use. Other examples are the chambers exposing samples to ultra-violet (UV) radiation, which are used to simulate the weathering effect of sunlight. There is also one example described by Hsu et al. [25] where the combined effects of abrasion (by a rubber blade scraper), weathering (by UV lamps) and wind (using a fan) are investigated.

Machining	Process	Nano-composite (Nano-objects)	Refs.
Abrasion	sandpaper pad	 PA+SiO₂ NP POM+CNT Cement+CNT Cement+CSH TPU+CNT 	[15] " " [20]
	Taber, rotary	 PA+SiO₂ NP POM+CNT Cement+CNT Cement+CSH TPU+CNT 	[15] " " [20]
		 PU+ZnO Clearcoat+ZnO Architect. coating+ZnO 	[12] "
		• Epoxy+CNT	[18]
	Taber, linear	• PMMA+Cu NP • Polycarb+CNT	[17] "
		• PET fabric + PVC coat + Nano-clay	[16]
Cutting	band-saw	 (CF+CNT) in epoxy (Alumina fibres + CNT) in epoxy 	[4] "
	disc-saw (wet)	 (CF+CNT) in epoxy (Alumina fibres + CNT) in epoxy 	[4] "
		CNF composite	[7, 19]
	mill	• Al-alloy	[32]
		None (Li-Ti-MO)	[27]
Drilling	concrete drill	Nano-Crete concrete (fumed silica)	[8]
	flute-reamer	Bismaleimide / Graphite (Cemented carbide)	[41]
	polycrystalline diamond drill	Bismaleimide / Graphite	[41]
	abrasive drill	 (CF+CNT) in epoxy (Alumina fibres + CNT) in epoxy 	[6] [5, 6]
EDM	tungsten electrode	• PMMA+CNT	[37, 38]
FSW	mill	• Al-alloys	[31]
Grinding	micro-grinder	• thermal spray coating (WC-12Co; Al ₂ O ₃ -13TiO ₂)	[40]
	grinder	Epoxy-CNF aerospace composite	[19]
		Granite Clay ceramic	[30]

 Table 3: Summary of machining processes and nanomaterials processed.

Machining	Process	Nano-composite (Nano-objects)	Refs.
		• Hardwood	
		None (Ag NP)	[28]
Laser	femto-second	None	[53]
Nano-mill	FIB	• PMMA+CNT	[39]
Sanding	manual	Epoxy+CNT Epoxy-CNF composite / CNF Buckypaper laminate	[14] [19]
	miniature	• PU-ZnO • AC-ZnO • AC-Fe ₂ O ₃	[13] "
	orbital	 PVA paint +TiO₂ Acryl paint + TiO₂ Acryl paint+CB UV Hardcoat + SiO₂ sol 	[10, 11] [11] "
	belt	• Epoxy-CNF aerospace composite	[19]
Turning	lathe	• Al-alloy, Mild steel, High tensile steel (tool: cermet)	[33, 34]
		• None (tool: Si ₃ N ₄ whiskers; TiN NP)	[35]
	CNC lathe	Carbon fibre reinforced composite (tool: WC; TiC)	[36]
Weathering	UV exposure	 PA+SiO₂ NP POM+CNT Cement+CNT Cement+CSH TPU+CNT 	[15] " " [20]
		• Epoxy+SiO ₂ • Epoxy+MWCNT	[24] "
		Photocatalytic paint+TiO ₂	[25]

4. METHODS IDENTIFIED TO ASSESS AND MEASURE THE RELEASE OF NANOMATERIALS FROM COMPOSITES OR OTHER ARTICLES

The range of on-line measurement equipment and particle collection-based off-line methods of sampling and characterisation has been well documented in recent reviews on the subject [1, 22, 59-61] possibly with the exception of instruments based on diffusion charging used for measuring ultra-fine particles [62, 63].

In terms of the use of real-time sampling equipment, there is to-date only one report of an investigation of a positive control, in terms of a nano-composite, which demonstrates that instruments used are in fact capable of detecting individual nano-objects with the required sensitivity [18]. However, It has been shown for aerosols generated synthetically by atomisation that common particle sizing equipment does have the required sensitivity for the detection of nano-objects [64, 65].

The determination of emissions from machining of composites requires the measurement of ultrafine, fine and above micron-sized particles at levels above the sensitivity of the measurement equipment used and discriminated from other particles in the background to be significant.

4.1 Factors Affecting Particle Measurement

4.1.1 DIFFERENTIATING EMISSIONS FROM BACKGROUND LEVELS OF NANOPARTICLES

Because ultra-fine particle size fractions are of interest as an indication that nanoobjects have been released as single objects or as small agglomerates, the main issue that authors have reported quite consistently as being a significant problem is that of ultra-fine particle background. These can originate as emission sources of widespread mechanisation such as diesel soot from combustion engines or copper nanoparticles from electric brushes in motors. Several authors [1, 8, 10, 15] have detected high levels of ultra-fine particles which they attributed to particle emissions from electric motors. Szymczak *et al.* [66] and Lioy *et al.* [67] showed that certain motors (with carbon brushes sliding over copper commutator contacts) tend to release significant amounts of ultra-fine particles. Cross-contamination is another possible source that should be considered for nanotechnology laboratories or manufacturing facilities of products containing nano-structured materials.

As condensates from high temperature processes typically form agglomerates of spherical nanoparticles (under homogeneous nucleation conditions), they are relatively easy to identify by electron microscopy and physico-chemical analysis. Their presence, however, makes an interpretation of results more difficult and time consuming because the much faster and cheaper real-time instruments have currently no provisions to eliminate background particles from the count of target particles.

It has nevertheless been possible to extract nano-object specific emissions information, e.g. by determining typical mode distributions of background particles and subtracting them from measurements [10, 11, 16, 30] or by keeping foreign particle background away from the process under investigation. The latter can be achieved by means of partial enclosures that are flushed with particle-free air [12, 14, 15, 18, 25, 32, 34] or by enclosing the whole experiment in a clean room [26] or particle-proof containment [10, 11, 13, 16, 17, 30]. McGarry et al [22] describe in detail how to differentiate the measurement of emitted engineered nanomaterials from background particles.

4.1.2 AGGLOMERATION OF NANOPARTICLES AND SECONDARY MORPHOLOGY

It is well known that solid ultrafine particles in particular have a strong tendency to form agglomerates that can be porous and are not spherical at all. In addition, manufacturers are increasingly working with nano-fibres such as carbon nanotubes (CNT) for which the propagation behaviour is in most cases dependent on the secondary morphology rather than the primary dimensions of the nano-fibre that is given by its diameter and length.

With the discovery of nano-fibres such as carbon nanotubes (CNT) or inorganic nanotubes from materials such as boron-nitride, the state-of-the-art knowledge in aerosol science is being confronted with a problem whereby fibres tend to form structures like tangles and pills. It is a typical property of such High Aspect Ratio Nanoobjects (HARN) to propagate in airstreams guided by the secondary morphology of tangles and pills, rather than by their primary dimensions of diameter and length. This secondary morphology determines how these nano-objects propagate in air, how they enter the lungs of people, and where they are deposited when breathed in.

In terms of measurement it is this secondary morphology that dominates the aerodynamic size of these nano-objects. In order to assess the size of these particles by their inertia, which is how impactors will see the object during detection, one has to take into account that these filigree structures are highly porous and that therefore, the material density of the object according to its visible volume is potentially only a few percent of the material density of its constituents. Similar to aerogel particles, the visible and aerodynamic diameters of these nano-objects will be significantly different from each other because the two diameter criteria have been matched by calibration using solid latex spheres, which have a much higher material density.

The formation and expression of the secondary morphology for a nano-fibre can vary greatly and depends on the circumstances under which it was formed. For example, when dispersed CNT are individualised by ultrasound [68], the nano-fibres can travel inside some of the liquid droplets of the aerosol. The shape of the secondary morphology of this CNT will be determined by the perimeter of the water droplet under the influence of evaporation. If CNTs have been embedded in a polymer matrix, those that are located near the material surface can be exposed to open air as the matrix material is degraded preferentially under the influence of UV radiation. Under these circumstances the secondary morphology will depend on how the CNTs were embedded in the matrix.

As a consequence it is generally not possible to describe the propagation behaviour of a nano-fibre by its geometrical dimensions such as the fibre length and its diameter. Instead it is necessary to take into account the secondary morphology of these nano-objects and keep in mind that they can morph into different shapes on the way.

4.1.3 TIERED APPROACHES TO ASSESSING RISK

A number of organisations have developed or proposed the use of three-tiered approaches to the measurement of nanomaterials emissions and exposures [69-72].

The three-tiered approaches vary in detail, but are generally based on:

Tier 1 - Occupational hygiene survey

Tier 2 - Number and mass concentration measurement using handheld instruments

Tier 3 - Follow-up evaluation, e.g. sampling for further assessment and comparison with exposure standards

It may not be necessary to undertake all three tiers if sufficient information is gained from the Tier 1 or from Tiers 1 and 2 combined.

4.2 Release Measurement by Mass, Surface Area and Number Count

Instruments discussed in this section quantify aerosolised particle loads by a single number of either mass, surface area or number count and are summarised in Table 6 of Appendix A.

4.2.1 MASS CONCENTRATION

Historically the most common measurements are those of mass concentration. They include the PM standards (PM_{10} and $PM_{2.5}$) that are used in legislated areas of air quality control and exposure monitoring.

Some optical particle measurement systems (e.g. DustTrak) provide mass concentration readings that are deduced from light scattering measurement so that it is possible to calculate an estimate for mass if the material density of the particles is known. Another type of mass measurement is represented by the carbon analysers, which detect any chemical compounds that contain carbon and separate those into elemental carbon (EC), e.g. fullerenes or carbon nanotubes, and organic carbon (OC) that includes the majority of other carbon compounds that are found in air.

4.2.2 SURFACE AREA

The measurement of surface area from objects contained in an aerosol has been investigated. Several authors pointed out the importance of this measurement metric for chemical processes on solid surfaces, such as catalytic conversion and chemical attachment to graphitic, activated carbon. This is because for certain structures, e.g. porous structures or nano-objects, the available active surface area can be significantly higher than suggested by the mass of the structure.

4.2.3 PARTICLE NUMBER COUNT

The measurement metrics used most frequently by far in conjunction with nano-objects is that of particle number count. This technique is much more sensitive to ultra-fine particles than measurement by mass because nano-objects can occur in very large numbers without making a noticeable contribution to mass.

The work-horse in particle number count is the condensation particle counter (CPC), which detects sub-micrometre particles and nano-objects of any kind down to diameters as low as 2.5 nanometres in some instances (e.g. TSI 3776, TSI 3786). It is also used, together with electrometers, in more sophisticated instrumentation that classifies particles according to their size, but the CPC itself does not discriminate particles within its detection range.

The suitability of CPCs to detect ultra-fine nano-objects of any kind is the underlying reason for this suite of instruments being used for a very broad range of nanomaterials. The fact that CPCs only count, and do not discriminate, has virtue. CPCs can operate at lower particle concentrations because they count over a much wider particle size range than particle sizing instruments (e.g. SMPS). This was a crucial capability in the case of detecting particle release from a Taber abrader [12] where release levels were too low for a statistically significant quantification by SMPS.

The most prominent nano-object additive to composites is carbon nanotubes (CNT). CPCs are capable of detecting CNTs reliably, but are unable to discriminate CNTs from other nanoparticles that are present in common particle background. Two ways to overcome this specific problem are to either exclude other particles by means of particle-proof enclosures or by combining CPC measurements with collecting nano-objects and analysing them, as discussed in Section 4.4.

A specific virtue of most instruments discussed in this section is their portability, ease of use and relatively low cost. NIOSH has made use of these favourable attributes by proposing the Nanoparticle Emission Assessment Technique (NEAT) [69, 73] that many hygienists and researchers have since used routinely in their investigations. The associated process involves conducting a preliminary assessment of the work environment using the portable equipment with the aim of identifying "hot spots" of potential emissions across a large area relatively quickly. These hot spots may be subsequently revisited in a more detailed investigation that involves more specific equipment and is generally more time consuming. Further details on this second type of equipment are provided in the following Section 4.3.

4.3 Particle Size Distribution and Chemical Composition

4.3.1 PARTICLE SIZE DISTRIBUTION

A number of instruments are used to examine particle size distribution in machining tests. The particle size range of operation for each type of particle-sizing instrumentation is listed in column three of Table 7 (Appendix A). On the coarse particle scale of measurement we have instruments like the Aerodynamic Particle Sizer (APS), the Laser Aerosol Particle size spectrometer (LAP) and various types of Optical Particle Counters/Sizers (OPC / OPS). On the ultra-fine particle end of the spectrum there are instruments like the Scanning Mobility Particle Sizer (SMPS), the Fast Mobility Particle Sizer (FMPS), the even faster Engine Exhaust Particle Sizer (EEPS) and the Diffusion Size Classifier (DiSC). Working fairly broadly across a large part of the particle size spectrum is the Electrostatic Low Pressure Impactor (ELPI).

The operating ranges of both groups of instruments overlap to some extent in the fine particle range, which is being used to construct instrument combinations that can work across the whole spectrum of particles from ultra-fine to coarse as a single instrument (Table 8).

The number of investigations listed in Table 7 suggests that combinations of SMPS or FMPS with APS are used very frequently, as are the CPCs listed in Table 6. Optical particle counters, part of NEAT, have been used less frequently in the investigation of machining. One possible reason for this observation could be the fact that most handheld OPCs have a low operating range that is limited usually to less than 100 particles per cm³, as specified by the coincidence loss limit of the instrument, though the portable OPC model 1.108 manufactured by Grimm operates in particle concentrations up to 2000 particles per cm³. This instrument has been used for a number of investigations discussed in this report [26, 27, 69, 73]. Another recent alternative to this type of instrument is the TSI 3330 OPS.

4.3.2 LOG-NORMAL PARTICLE MODES

The diameters of particles that originate from a specific generation process tend to be distributed according to a log-normal distribution [74], but only few studies have undertaken a detailed analysis of measurements in terms of these distributions. Koponen *et al.* [10, 11] analysed particle emissions from a hand-held sander and found that it was possible to describe the PSD highly accurately by means of 5 log-normal modes. By having a mathematical description of the particle background released by the sander alone, it was possible to eliminate this effect from the PSD spectra obtained from sanding of polymeric coatings that contained nanoparticles. Koponen found that modes centred in a typical range of 130 nm to 180 nm were most likely representing particles released from the process of sanding the coatings. Schlagenhauf *et al.* [18] have identified in their mode analysis involving a CNT-epoxy composite a shift from 70 nm to 90 nm in the first mode (out of four). Similarly, Pfefferkorn *et al.* [31] identified a mode centred near 30 nm particle size could be attributed by chemical analysis with high probability to contamination originating from lubricants used in machining (not related to FSW machining process).

4.3.3 CHEMICAL COMPOSITION

While particle size distributions can provide highly useful information on the characteristics and number of the sources for particle release (mode), an important dimension in identifying the origin of the source and quantification of emissions is analysing the chemical composition of pertinent particles (Table 9). This can be achieved in semi-real-time by Diesel Particulate Matter analysers (DPM) where the elemental carbon (EC) fraction that is made up of diesel soot is segregated from the organic carbon (OC) fraction of most other carbon-based chemical compounds. This technique is also applicable to carbon nanotubes (CNT). Other real-time instruments such as the photoelectric aerosol sensor (PAS) are portable and sensitive to polycyclic aromatic hydrocarbons PAH [6] but not highly specific, while real-time particle mass spectrometers (no references included in this review) are highly specific but very complex, delicate to operate and extremely expensive in the initial purchase.

As practical real-time solutions for chemical analysis are still in development, it will be necessary in most cases to conduct such investigations on airborne particles by means of relatively time consuming off-line techniques. These are discussed in Section 4.4.

4.4 Aerosol Characterisation by Analysis of Collected Particles and Nano-Objects

The technique of collecting particles for subsequent analysis has long been used. However, with the increasing use of nanotechnology there is a need to be able to collect such nanoparticles for off-line analysis by a suite of sophisticated equipment that is unable to analyse particles and nano-objects directly from an airstream. Some of these techniques are summarised in Table 10 (Appendix A).

Because particles and objects released by machining of nano-composites are potentially of nanoscale it is necessary to use collection equipment that is suited for presenting such objects to the analysing equipment without change of the relevant characteristics. This can be achieved by sampling "cassettes" that contain membranes for stripping solid aerosol objects from an airstream that passes through the membrane, by diffusion cells that collect ultra-fine particles on open mesh structures (PWRAS), by inertial impactors that deposit particles dynamically onto solid target surfaces (ELPI, PWRAS) as well as by thermophoretic (TP) or electrostatic precipitators (ESP, NAS) that achieve the same using thermal gradients or electrostatic attraction, respectively. Large particles can be collected by simply letting them fall into a particle storage container under the influence of gravity [24].

In terms of membrane materials that are particularly suited to the requirements of nanotechnology there are the relatively novel polycarbonate membranes. They are characterised by very smooth and clean surfaces that appear flat on a nanoscale and are equipped with prominent and well-defined cylindrical pores. They work as surface filters where particles are predominantly deposited on the membrane surface and less so inside the pores. Sample preparation methods such as ISO 14966 for SEM [75] have been designed to work with these membranes. On the other hand, more conventional membranes such as mixed cellulose ester (MCE) have a sponge-like

structure where aerosol particles can be captured inside the tortuous pores as much as they are captured on the membrane surface. In this case, sample preparation methods NIOSH 7400 for phase-contrast microscopy [76] or NIOSH 7402 for TEM [77] can be used for imaging collected objects.

Special caution must be applied when using plasma etchers or ashers for the purpose of removing organic material from the membrane surface when carbon nanotubes (CNT) are the target nano-objects [78]. While CNT are chemically fairly resilient, e.g. in comparison to polymeric matrix materials, they are affected significantly by such plasmas and eventually destroyed. Direct deposition onto carbon-backed TEM grids by a precipitator or a diffusion cell with suitable grid holders is preferable in this case, particularly if the structures are porous or complex in shape.

Where samples have been prepared for inspection by electron microscopy it is usually possible to obtain additional information on the chemical composition - for elements heavier than carbon - by means of Energy Dispersive X-ray (EDX) spectroscopy, which is commonly available with most SEM or TEM systems. More sophisticated systems, such as the TEM used in [27], have the capacity to generate "elemental maps" whereby the two-dimensional electron imaging facility is coupled with EDX spectroscopy to reveal the position of specific, selectable elements on the particle surface.

Increased surface selectivity can be achieved using X-ray Photoelectron Spectroscopy (XPS), which is important in terms of suppressing unwanted disturbances such as the signature of the sample substrate. Secondary-Ion Mass Spectroscopy (SIMS) is very selective in determining differences in the composition of organic compounds and is even more sensitive than XPS in the detection of trace elements [15]. Other alternative techniques that have been used are Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) [5, 6] and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) [27, 31].

To determine the existence or non-existence of un-agglomerated, free nano-objects, most investigations have focused on using electron microscopy (SEM, TEM) to find and identify them. So far, only three studies have identified the existence of free reinforcing nano-objects released during machining, for CNT [18], for nanoclay [79] and for CNFs [19]. Wohlleben *et al.* [15] have taken a different approach in their investigations, where they dispersed abraded material from experiments in water and ethanol with the aid of ultrasound, followed by a colloidal analysis using laser diffraction (Malvern Master Sizer) or Analytical Ultracentrifugation (AUC). A summary of releases detected and identified is provided in Table 2 of that reference. Normal use (abrasion) produced no release for any of the nano-composites tested, while weathering of POM with CNT led to exposed CNT attached to the surface. Use of sandpaper on a stub was the most potent release scenario for the Cement 1 – CNT composite, where large fragments with protruding CNT were found on the surface (Fig. 5d in [15]). Sachse *et al.* [9] performed similar investigations in the liquid phase for nanoclays.

5. EMISSION LEVELS AND TYPES OF EMISSIONS RESULTING FROM MACHINING PROCESSES

Results were examined from the following viewpoints:

- Machining processes and parameters: which ones lead to higher levels of emissions?
- Types of composites: do release levels depend on the type of matrix or reinforcing nano-object or both? How does a composite containing nanomaterial (NM) differ from a composite without NM in response to machining?
- Mass and number concentration: what are typical release levels?
- Relationship between release and constituents: Do emissions contain nanoobjects, matrix fragments or combinations? Have chemistry or morphology been changed?
- Emission controls: how effective are they?

Details of experimental findings on emissions from machining are given in Tables 11 to 13 in Appendices B to D. Matrix materials examined include epoxies, polymers, cementitious mortars and less conventional materials such as thermal spray coatings or cermets used for high-performance machining tools. The types of reinforcing nano-objects used include nanoparticles, nano-fibres (CNT, CNF and inorganic whiskers), nano-platelets (clays) and colloid suspensions (sols).

For the machining processes, real time measurements and observations made from investigating collected particles by electron microscopy (or other off-line analysis) are reported.

A database (Microsoft Access) of emission measurements from machining has been developed that is available as a supplement to this report [80]. The database is particularly helpful with categorizing and grouping of data sets for comparison.

5.1 Mass concentrations

Mass concentration measurements for a range of composites containing carbon nanotubes are shown in Figure 1. The matrix material was epoxy in each case, but the composite structures had different levels of complexity.

The intrinsic particle release from manual sanding, as measured inside a biosafety cabinet [14], can very low and is depicted in Figure 1 as 'Sand.Man.Epoxy'. For manual sanding without engineering controls, the respirable mass concentration was estimated using OPC data to be 0.011 mg m⁻³ at source and 0.003 mg m⁻³ in the breathing zone [14]. These levels are significantly lower than for high energy dry cutting. Respirable mass concentrations were 0.021 mg m⁻³ when working in a custom fume hood, which was not effective for this work and actually increased potential exposure. When hand sanding was undertaken inside a ventilated booth [19], the concentrations measured were 3.09 mg m⁻³ with vent off and 0.16 mg m⁻³ with vent on (depicted in Figure 1 as 'Sand.M-Bth.CF-Lam'). Levels of particle release could have been elevated in this

particular setting for two reasons: 1) These measurements were conducted in an industrial environment where cross-contamination from other processes, such as transfer of loose CNF, may occur. 2) The sanding involved a laminate made up of CNF-Epoxy composite and CNF Buckypaper layers, where CNF in the Buckypaper are only held together by Van der Waals forces and therefore easily disrupted.



Figure 1: Measured mass concentrations of particles during the machining of composite materials containing carbon nanotubes and carbon nanofibres. Refer to Table 13 for measured values.

Key:

Background: Mass concentration of background particles with no machining occurring **Control**: Mass concentration in air during the machining of composites without carbon nanotubes or nanofibres

Composite: Mass concentration in air during the machining of composites containing carbon nanotubes or nanofibres

Belt sanding ('Sand.Belt.CF-Epoxy') produced a mass concentration of 18.5 mg m⁻³ at source [19], which was the highest level of release reported from all processes in terms of mass concentration.

Surface grinding ('Grnd.CF-Epoxy') produced a mass concentration of 0.90 mg m⁻³ at the edge of the LEV inlet and 0.50 mg m⁻³ in the worker's breathing zone [19].

Taken together, the results show that not all the engineering controls used were fully effective in minimising potential exposure. Emission levels are in many cases higher

than background levels and significantly higher for high energy machining such as cutting, grinding and motor-driven sanding.

For high energy dry cutting using a band-saw labels 'Cut.BS.AI-Epoxy' and 'Cut.BS.CF-Epoxy'), airborne concentration levels of released particles were higher at the source than in the operator's breathing zone [4], with respirable mass concentrations up to 8.36 mg m⁻³ at source.

In the study by Bello et al [4] emissions resulting from wet cutting using a disc saw ('Cut.DS.CF-Epoxy') were not statistically different from background levels, except when the cutting wheel guard was damaged (for the control material). However, in the study by Methner et al [19], emission levels for a wet saw cutting process were 5.75 mg m⁻³ at source with no controls, and 1.13 mg m⁻³ in the breathing zone when the sawing process was undertaken inside a ventilated booth. Release generated by band-saws and disc-saws may not be that different.

5.2 Particle number concentrations

Number concentration measurements for CNT-containing composites are shown in Figure 2. The bar graph distinguishes by colour the total concentration of particles measured in the background (grey) from the total concentrations measured for the machining of matrix material with nano-objects (Composite: red) and without nano-objects (Control: green). Release data from the composite are covering up data from the control and background where they overlap. Measurements were read from pertinent instruments as reported and do not take into account the chemical composition (Section 4.3.3) or morphology (Section 4.1.2) of the particles.

Results suggest that the processes of grinding (label 'Grnd.CF-Epoxy'), cutting ('Cut.'), drilling ('Dril.) and motor-powered sanding ('Sand.Pad.POM') generate the highest levels of particle release, while release concentrations from abrasion processes ('Abr.') or manual sanding ('Sand.Man.Epoxy') are comparably lower. Emissions from high energy processes are higher than typical particle background, but those of low energy processes can disappear in the background if no suitable precautions are taken ('Sand.Man.Epoxy', 'Abr.Polycarb'). Results from [4] showed no significant difference in particle number concentration between samples containing CNTs and controls.

Looking at the lower boundaries of background measurements across cutting, drilling and abrasion experiments, there is a fairly common value ranging within about 2000 – 3000 particles/cm³. Air-conditioned buildings, laboratories and offices typically carry this level of background particles under normal conditions. The use of local exhaust ventilation (LEV) or specifically designed enclosures can reduce particle background below this range. The effect of such systems can be gauged from the results of the sanding experiments [14, 15] and the abrasion test for polycarbonate 'Abr.Polycarb' [17].

High speed dry drilling produced higher levels of particle number concentrations than low speed dry drilling [6]. However, high speed wet drilling produced levels that were an order of magnitude lower than low speed dry drilling. As with dry cutting, dry drilling gave peak number concentrations above 10⁶ cm⁻³ in some cases [6]. Manual sanding and abrasion processes may differ notably from high speed cutting and drilling and higher energy sanding in that they produce significantly lower airborne particle number concentrations [14, 15, 17].

Tasks such as surface grinding of composite material produced substantial increases in particle number concentration (range = 4.2×10^4 to 4.9×10^5 cm⁻³) [19].



Figure 2: Measured number concentrations of particles released during the machining of composite materials containing carbon nanotubes and carbon nanofibres. Refer to Table 13 for measured values.

Key:

Background: Number concentration of background particles with no machining occurring **Control**: Number concentration in air during the machining of composites without carbon nanotubes or nanofibres

Composite: Number concentration in air during the machining of composites containing carbon nanotubes or nanofibres

Release investigations by number count on composite materials and coatings containing silicon dioxide, including fumed silica, produced results summarised in Figure 3. The abrasion experiment on polyamide 'Abr.Rot.PA' and the pad sanding 'Sand.Pad.PA' [15] both exhibit particle backgrounds that are typical of conditioned rooms. In this case, the release from nano-object free controls (green) is lower than release from nano-object containing composites (red), but the measured differences are small.



Figure 3: Measured number concentrations of particles during the machining of composite materials containing silicon dioxide nanoparticles or fumed silica. Refer to Table 13 for measured values.

Key:

Background: Number concentration of background particles with no machining occurring **Control**: Number concentration in air during the machining of composites without silicon dioxide nanoparticles or fumed silica

Composite: Number concentration in air particles, during the machining of composites containing silicon dioxide nanoparticles or fumed silica

Orbital sanding of hardcoat laquer 'Sand.Hardcoat' and of outdoor acrylic paint 'Sand.Outdoor' [11] was conducted inside an enclosure at reduced particle background. Measurements for the orbital sanding show clearly elevated values relative to particle background.

The background level for concrete drilling 'Dril.Concrete' [8] is about one order of magnitude higher, in line with being an outdoor setting, and varied strongly between investigations. In the case of measurements related to drilling, the background was 7,605 particles/cm³.

Release measurements for composites and coatings containing titanium dioxide nanoobjects are summarised in Figure 4. This data set contains results from investigations on particle release from weathering 'Wea..Paint.' under the influence of wind (represented by a fan) and mechanical friction (represented by the scraping action of a rubber blade) [25]. The release generated under those circumstances appears to be about three orders of magnitude lower than that from sanding or cutting of nanocomposites. Results from sanding suggest that adding TiO₂ nanoparticles may change release properties of surface coatings [11], with most but not all measurements being higher than for the controls. No control data were provided for cutting or weathering.

There is a cluster of data on measured particle release from the sanding of painted surfaces, results of which are depicted in Figure 5. Different types of paint bases including acrylic (Acryl.), polyvinyl acetate (PVA) were used polyurethanes (PU) as well as less specific compounds such as architectural coatings (Arch.), outdoor paints (Outd.) and hard-coat lacquers (Lacq.). The types of nanoparticles added include titanium dioxide (TiO₂), silicon dioxide or silica (SiO₂), zinc oxide (ZnO), carbon black (CB), iron oxide (Fe₂O₃) and Kaolin.



Figure 4: Measured number concentrations of particles during the machining of composite materials containing titanium dioxide nanoparticles. Refer to Table 13 for measured values.

Key:

Background: Number concentration of background particles with no machining occurring **Control**: Number concentration in air during the machining of composites without titanium dioxide nanoparticles

Composite: Number concentration in air during the machining of composites containing titanium dioxide nanoparticles

Particle concentrations generated by the sanding were found to lie within a range of 10^4 to 10^6 particles/cm³. These levels of particle release are fairly high and naturally occurring background particles were therefore of lesser significance. The main difficulty that the authors needed to overcome in their experiments was the enormous level of particles generated by the sander itself. It is suggested that these may originate from the motor, the abrasive paper and other moving parts of the sander. The values used

in the bar graph of Figure 5 have all been corrected to exclude particles from the sander. Koponen *et al.* [10] determined the total number concentration released by their orbital sander to be in the order of $3 \cdot 10^6$ particles/cm³, which is above the upper limit of particles released by the material itself. They used a particle mode analysis to eliminate emissions of the sander from their results. Göhler *et al.* [13] built a small hood to enclose the sanding wheel and material surface during the sanding process and aerosol samples were taken from within that hood.

The level of particles released by the sanding was lowest for the acrylic paint with titanium dioxide and highest for the hard-coat lacquer with silica particles. It seems that an addition of nanoparticles to these two paints had the effect of reducing the number of particles released by the sanding, which was quite significant for the hard-coat lacquer and less pronounced for the acrylic paint. All other paints in between showed either no significant change in the number of particles released or a slight increase when nanoparticles were added.



Figure 5: Measured number concentrations of particles released during the sanding of painted surfaces. Various types of paint with different types of nanoparticles were investigated. Refer to Table 13 for measured values.

<u>Key:</u>

Background: Number concentration of background particles with no sanding occurring **Control**: Number concentration in air of particles released during the sanding of painted surfaces without nanoparticles

Composite: Number concentration in air of particles released during the sanding of painted surfaces containing nanoparticles

5.3 Effect of machining parameters

Bello et al. conducted detailed investigations on cutting [4] and drilling [5, 6] of CNT-composites and made the following general observations:

- For cutting, the particle production was found to increase with the thickness (or number of plies) of the composite sample.
- For drilling, high speed drilling on dry samples and larger drill bits produce higher number concentrations.
- Use of lubricants reduces emissions arising from both cutting and drilling. This is demonstrated by comparing wet cutting and dry cutting results in Table 13.
- Drilling generated white fumes of ultra-fine particle condensate.
5.4 Particles emitted

A summary of emitted particles measured is shown in Table 4 below, with further details in Table 11 (Appendix B).

Table 4: Summary of emitted particles

[]+suppl.: Indicates that some information is provided in a supplementary document.

Machining Process (Tool)	Particle Source (Nano-objects)	Sampler: Description of exposure	Study
Abrasion (<mark>sandpaper</mark>)	Composites: • PA+SiO ₂ NP (SiO ₂) • POM+CNT (CNT) • Cement+CNT (CNT) • Cement+CSH (CSH)	Powders generated have Ø of several μm (10-80μm). • POM only: >400nm • POM+CNT: >700nm • CEM+CNT: >130nm	[15] + suppl.
Abrasion (Taber rotary)	• Epoxy+CNT (CNT)	Wide-range PSD made up of four modes: 326415nm; ≈680nm; ≈1200nm. 23002400nm. Found matrix particles, CNT protruding, free- standing CNT and agglomerates of CNT.	[18]
Abrasion (Taber linear)	 PET fabric + PVC coat + Nano-clay (Nanoclay) 	Peak of Ø-modes: • PET: 80 nm • PET+PVC: 80 nm • PET+PVC+ Nano-clay: 50 nm	[16]
	Composites: • PMMA+Cu NP (Cu) • Polycarb+CNT (CNT)	TEM images of <u>PC-CNT</u> : NP found, but no CNT. <u>PMMA-Cu</u> : Cu found in particles of µm Ø, Cu nearly detached from matrix.	[17]
Cutting (band-saw)	Composites: • [CF+CNT] in epoxy • [Alumina fibres + CNT] in epoxy (CNT)	 Abundance of 10-20 nm particles (spherical, agglomerated). Fibres of 30nm to 6µm Ø. Amongst fibres of 300nm Ø are several that are 10 µm long. No free CNTs. 	[4]
Cutting (Wet, via diamond disc saw)	Composites: • Epoxy coated CNF (CNF) • CNF composite material (CNF)	 Ø 30 nm to 200 nm dominant. Ø>400nm from wet-saw cutting. Ø≈500nm from CNF. 	[7]
	• Epoxy-CNF aerospace composite	 Matrix fragments. Substantial amounts of CNF, some free CNF. CNF agglomerates & bundles. 	[19] + suppl.
Drilling (drill press)	Composites: • [CF+CNT] in epoxy (CNT) • [Alumina fibres + CNT] in epoxy (CNT)	 Aggregates of respirable particles: CNT aggregates. spherical <10nm fraction: is condensate from white smoke. HARN fibres, few with nanoscale diameter. 	[6]

Machining Process (Tool)	Particle Source (Nano-objects)	Sampler: Description of exposure	Study
Drilling (hand held)	Bulk: Cement+SiO ₂ fumed (SiO ₂)	Median of particle Ø 37-51 nm; range 19 - 300 nm.	[8]
Grinding (<mark>stone whee</mark> l)	• Epoxy-CNF aerospace composite	 Matrix fragments. High concentrations of ultra-fine particles, but only few are CNF – some free CNF. 	[19] + suppl.
Sanding (<mark>manua</mark> l)	Composite: •CNT-enforced epoxy (CNT)	 TEM shows large particles of >300nm size with CNT protruding. No free CNT observed. 	[14]
	• Epoxy-CNF composite / CNF Buckypaper laminate	Evidence of CNF found (regardless of ventilation conditions).	[19] + suppl.
Sanding (miniature sander)	Polyurethane (PU) or Architectural Coatings (AC): • PU-ZnO (ZnO) • AC-ZnO (ZnO) • AC-Fe ₂ O ₃ (Fe ₂ O ₃)	SEM images suggest mass loss is dominated by $Ø > 20\mu m$. Abraded surface coating is source for coarse and fine particles (no abradant present).	[13]
Sanding (belt sander)	• Epoxy-CNF aerospace composite	 Matrix fragments. Few nanoscale CNF but no free CNF detected. Clusters of spherical carbon particles. 	[19] + suppl.

Dry cutting of composites containing MWCNTs generated statistically significant quantities of nanoscale and fine particles for a range of composite types (CNT–carbon, CNT–alumina, control) [4]. Submicron length fibres with nanoscale diameter and larger respirable fibres were also generated. The finest individual nano-fibres collected on TEM grids were about 30nm in diameter and several hundred nm long (Fig 8C and 8F in [4]). The authors stated that these were most likely fragments of carbon-fibres from the composite. No evidence was found of free MWCNTs being emitted.

For composites containing MWCNTs, differences were observed in the emissions from solid core drilling [6] when compared to the cutting [4] in size distributions, fibre concentration and particle morphology. In addition, clusters of CNT aggregates were observed by TEM during the core drilling.

In studies of the machining of CNT-containing composites, TEM showed large particles with CNT protruding, but no free CNT were observed [14]. A further study reported nanoparticles being emitted, but no isolated CNTs being found [17].

Twelve (12) out of 13 samples taken during the machining of CNF composites, examined by TEM, indicated that releases of free CNFs occur [19]. The majority of samples contained mostly unagglomerated CNFs, whereas a smaller subset of samples contained a larger amount of loosely agglomerated CNFs.

In summary, the following types of particles have been found to be emitted during machining of composites containing nanoparticles:

- Particles of matrix with reinforcing nano-objects embedded.
- Emitted nanoparticles have been identified. These primarily come from matrix, but emitted reinforcing nanoparticles have been identified.
- Free CNTs have been identified amongst emitted particles in only one case [18] involving abrasion but not in other studies of machining of CNT-containing composites. Free CNFs were emitted during the machining of a CNF-containing composite [19].
- CNT aggregates have been found to be emitted during drilling [6] and abrasion [18].
- Examples of nano-objects protruding from polymeric particles have been observed, including CNT in epoxy [14], zinc oxide nanoparticles in white pigmented architectural coating [12] or in polyurethane [13], and copper nanoparticles in PMMA [17].

5.5 Conclusions

- 1. The levels of particle emissions detected on-line from composites containing nanoobjects as reinforcement are not significantly different to composites without nanoobjects.
- 2. High energy processes emit significantly higher numbers of particles and produce higher airborne mass concentrations than low energy processes.
- 3. Significantly lower emissions occurred for wet machining in comparison to dry machining during studies conducted by Bello et al [4, 6]. However, wet saw cutting has also been shown to produce significant levels of emissions [19].
- 4. Predictions on the rate of emissions depend on numerous factors. However, currently there is insufficient data to arrive at any conclusions about how emissions vary with material composition.
- 5. A combination of nanoparticles (primarily from matrix, but also free reinforcing nano-objects) and matrix particles with nano-objects embedded are emitted.
- 6. As for emissions control generally, engineering controls can be used for machining processes to minimise and sometimes prevent worker exposure. Evidence has shown the criticality of ensuring that controls are maintained properly and that they are designed appropriately for the task.

6. DISCUSSION OF RESULTS

In order to assess the particle release data from Table 13 (Appendix D) it is useful to have some reference values, or particle control values, to assess emission levels. The term 'particle control value' is used to refer collectively to different types of exposure standards and exposure limits. For chemicals in Australia, regulated particle control values are the Workplace Exposure Standards [81]. Particle control values for nanomaterials have been examined in a number of studies, including by McGarry *et al.* [22], the British Standards Institution [82] and Benke *et al.* [83]. A selection of particle control values for nanomaterials and nanoscale particles, implemented and proposed, are listed in Table 5 below.

Table 5: List of particle control values for nanomaterials and chemicals containing nanoscale particles and related substances.

Chemical	Particles	Value Type	Particle control value * 8-hour TWA ** 10-hour TWA	Unit	Reference
Aluminium - dust - welding fumes	Al alloys. Some fraction of welding fume is nanoscale.	WES	10* 5*	mg/m ³ mg/m ³	SWA, Hazardous Substances Information System (HSIS) [84]
Fibre-like objects	Asbestos Synthetic mineral fibres	WES	0.1* 0.5	fibres/ml fibres/ml	HSIS [84]
Carbon black	Carbon black Many forms are nanoscale	WES	3*	mg/m ³	HSIS [84]
Carbon nanofibres or nanotubes	CNF, CNT CNT	Proposed REL BEL	0.007 0.1 0.01	mg/m ³ fibres/ml fibres/ml	NIOSH [85] [83] [82]
Fullerenes	e.g. C ₆₀	Proposed EL	0.39	mg/m ³	AIST [86, 87]
Fumed silica	SiO ₂ Primary particle size is nanoscale	WES	2*	mg/m ³	HSIS [84]
Titanium dioxide - bulk: - fine: - ultrafine:	TiO ₂	WES REL REL	10* 2.4** 0.3**	mg/m ³ mg/m ³ mg/m ³	HSIS [84] NIOSH [88] NIOSH [88]

Key: WES – Workplace exposure standard REL – Recommended exposure limit BEL – Benchmark exposure level EL – Exposure limit

For reference, the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) for poorly soluble particles not otherwise specified is 3 mg m⁻³ (respirable particles) and 10 mg m⁻³ (inhalable particles).

6.1 Comparing emissions with particle control values

There are three categories of particles emitted:

- 1. Particles of matrix, some with nanoparticles embedded. These form a very significant fraction of particles emitted
- 2. Free nano-objects mostly nanoparticles from the matrix, but free reinforcing nanoobjects have been identified
- 3. Agglomerates and aggregates of nano-objects

The comparison of emission measurements and particle control values is not straightforward due to several reasons:

- Quantitative measurement from on-line instruments is insufficiently particle-specific. Because emissions are often a mixture of particles of interest with other particulate emissions and background particles it is difficult to draw any firm conclusions by comparing those emissions with the particle control values in Table 5.
- The effect on toxicity of nano-objects embedded in matrices is not known in detail. The exposure standard for the matrix material or the nano-objects assumes that particles were formed from a specific material and not the combination thereof. The question arises furthermore as to whether the reinforcing nano-objects may be released from the matrix in the body after inhaling.
- Free nanoparticles and agglomerates can be compared with nanoparticle exposure standards but there are not many in place.

Noting that cutting processes may last for less than 1 minute, dry cutting produced a respirable mass concentration of up to 8.38 mg m⁻³ [4] and belt sanding 18.50 mg m⁻³ near the source [19]. While the toxicity of particles released is uncertain when the emission consists of a mixture of particles, these mass concentration levels are significant when considering, for example, the ACGIH TLVs for poorly soluble particles not otherwise specified. Respirable fibre levels for the dry cutting of CNT-alumina composites were 1.6 fibres cm⁻³ at source and 0.2 fibres cm⁻³ in the operator breathing zone [4]. For comparison, workplace exposure standards for specified fibres are 0.1 fibres cm⁻³ for all forms of asbestos and 0.5 fibres cm⁻³ for ceramic fibres, man-made mineral fibres, superfine glassfibre, synthetic mineral fibres (ceramic fibres, glasswool and rockwool).

6.2 Potential risk to health

Significant quantities of material can be released from composites containing nanoobjects by high energy machining processes. Similar quantities of material are released from composites that do not contain reinforcing nano-objects. In the absence of effective engineering controls, operators of high energy machining tools may be exposed to (a portion of) the emitted particles. Whilst a mixture of particles and particle sizes is emitted, and thus the overall toxicity is difficult to estimate, reference to ACGIH TLV values for poorly soluble particles not otherwise specified suggests that a potential health risk exists, irrespective of the composition of the mixture.

Particle characterisation has shown the presence of significant quantities of nanoparticles from high energy machining, primarily from the matrix. In addition, the presence of free fibres of various types, including carbon nanotubes in one study [18] and carbon nanofibres [19], has been identified amongst particles emitted.

In the recent report *Human Health Hazard Assessment and Classification of Carbon Nanotubes*, the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) recommended that carbon nanotubes should be classified as hazardous unless evidence for the specific form of the material indicates otherwise [89]. The recommended classifications in accordance with the *Approved criteria for classifying hazardous substances* (Approved Criteria) [90] and the *Globally Harmonised System of Classification and Labelling of Chemicals* (GHS) [91] are:

Carcinogenicity

- Approved Criteria Classification: Carcinogen Category 3, Harmful (Xn). Risk Phrase: R40 Limited evidence of a carcinogenic effect
- GHS Classification: Carcinogen Category 2. Hazard Statement: Suspected of causing cancer

Repeated or prolonged inhalation exposure

- Approved Criteria Classification: Harmful (Xn). Risk Phrase: R48/20 Danger of serious damage to health by prolonged exposure through inhalation
- GHS Classification: Specific target organ toxicity following repeated exposure Category 2. Hazard Statement: May cause damage to lungs/respiratory system through prolonged or repeated inhalation exposure

Recommendations on controls to use when machining products containing carbon nanotubes are provided in *Safe handling and use of carbon nanotubes* [92].

Thus, while taking into consideration that machining processes such as high energy cutting are of short duration (typically less than one minute per task), it is concluded that high energy machining of composites containing reinforcing nano-objects presents

a health risk. The use of well-maintained engineering controls to minimise exposure is recommended.

Lower energy machining processes generally emit significantly lower levels of material. For manual sanding of CNT-reinforced epoxy composite without controls, the respirable mass concentration was estimated using OPC data to be 0.011 mg m⁻³ at source and 0.003 mg m⁻³ in the breathing zone, but the intrinsic concentration of particles generated by the process (with interfering background particles eliminated) could be as low as 10⁻⁴ mg m⁻³ [14]. These levels of emissions should not present a significant health risk if low toxicity particles are emitted, but do present a health risk if emitted particles are biopersistent fibres or otherwise have high toxicity. For the study above [14], particles larger than 300nm with CNT protruding, but no free CNT, were observed in TEM images. In another study involving hand sanding of a CNF-composite inside a ventilated booth with vent off, and where the measured mass concentration of released particles was 3.09 mg m⁻³, free CNFs were identified in TEM images [19].

The duration that particles and nano-objects remain suspended in the air after the machining process has stopped is of significance to staff who continue working in the vicinity of the process area. While coarse particles are settling on the floor after a relatively short period of time, it has to be noted that respirable particles (in the submicrometre range) remain suspended for significantly longer times. Active and effective extraction is required to remove these from the surroundings of the processing area.

7. OUTLINE OF RESEARCH NEEDS, CONSIDERING CURRENT KNOWLEDGE AND CAPABILITIES

7.1 Measurement

Several authors have called for a more harmonised and standardised approach within the international community to develop methods for assessing the effects of use and wear on nano-composites [1, 13]. In the context of life-cycle based economic assessments, it is important to continue work on standardised commercial test methods such as the Taber abraser. What is missing for this particular instrument is a particle-proof enclosure that allows particle emissions from the abrasion process to be investigated without effect or bias from other sources. Further improved simulations of wear and weathering effects acting individually or in parallel, as described by Hsu et al. [25], should also be developed in order to ensure that these sorts of testing and assessment practices are adopted more widely and on an international basis.

7.2 Data

Further data required includes:

- Particle-specific quantitative measurements of emissions to be able to assess emissions against particle control values
- Further work to confirm whether free CNTs and CNFs are released from machining of CNT-based composites
- Biopersistence testing of particles of matrix containing carbon nanotubes used for reinforcement

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APPENDIX A – MEASUREMENT TECHNIQUES

Table 6: Summary of measurement methods used to measure mass concentration, surface area and number count from the release of particles or nano-objects.

Release Meas.	Model	Range / Analysis	Ref
Mass	concentration		
DPM	NIOSH 5040		[7]
OPC-RPM	Grimm 1.108	300-20,000 nm	[14]
PM ₁₀	DustTrak 8520	0.1-10 mg/m ³	[4, 6, 7]
PM _{2.5}	DustTrak 8520	100-2500 nm	[31, 33, 34]
PM _{1.0}	DustTrak 8520	100-2500 nm	[21, 29]
	DustTrak DRX 8533	100-15,000 nm	[19]
Surface	area		
DC	Echo-Chem, DC 2000-CE	to 1000 fA	[6, 7]
NSAM	TSI 3550	10-1000 nm	[23, 31]
Number	count		
CPC	TSI 3007	10-1000 nm	[4-7, 14, 23, 27, 31]
	TSI 3022 with diluter	6-3,000 nm	[13]
	TSI 3022	6-10,000 nm	[12]
	TSI 3022A	7-3,000 nm	[30]
	TSI 8525 (P-Trak)	20-1000 nm	[29, 31]
	Grimm 5.403	4.5-3,000 nm	[16, 26]
CPC / OPC	TSI 8525 (P-Trak) ART-MetOne HHPC-6	20-300 nm	[19]

Table 7: Summary of measurement methods used to characterise particle size distributions from releases of particles or nano-objects.

Release Meas.	Model	Range / Analysis	Ref
APS	TSI 3320	523-20,500 nm	[30]
	TSI 3321	500-20,000 nm	[4, 6, 18, 31, 32]
	TSI 3321 with 100:1 diluter TSI3302A	542-19,810 nm	[10, 11]
	Not specified	500-20,000 nm	[33]
LAP	Topas 321	300-30,000 nm	[13]
DiSC	Philips NanoTracer	10-300 nm (Adv mode)	[8]
EEPS	TSI 3090	5.6-560 nm	[31]
ELPI	Dekati	30-10,000 nm	[7]
		Polycarb. mem./stage 2	[17]
FMPS	TSI 3091	5.6-560 nm	[4, 6, 11, 13, 23]
OPC-NC	Grimm 1.108	300-20,000 nm	[27]
	TSI 8220 Aerotrak	300-10000nm max 74 pp/cc	[29]
	MetOne HHPC-6	300-10,000nm max 74 pp/cc	[29]
SMPS	TSI 3034	10-487 nm	[29]
	TSI 3071A	CPC 3022 14-820 nm	[15]
	TSI 3080	N-DMA 4.2-100 nm	[30]
		L-DMA, CPC 3775: 13-573nm	[18]
		L-DMA 15-661 nm	[25]
		L-DMA 10-736 nm	[32]
	TSI 3934	16-626 nm	[12]
		L-DMA 60-777 nm	[30]
	TSI 3936	L-DMA 15-673 nm	[21, 23]
	Grimm 5.5-300	M-DMA 5-300 nm	[16]
	HCT EPS 4410	L-DMA 15-700 nm	[28]
	Not specified	2.5-1000 nm	[33]
WRAS	Grimm OPC 1.108	5-20,000 nm	[26]

Instruments combined	Manufacturer	PSD interface (nm)	PSD range	Studies			
Wide Range Instruments for Real-time Measurements							
WRAS: DMA 5.500 + CPC 5.400 + AS 1.108 / 1.109	Grimm	300 - 350	5-32,000 nm, < 10 ⁷ pp/cm ³	[26]			
SMPS (N&L) + APS 3320	TSI	60 - 100 523 - 777	4.2-20,500 nm 10 ⁷ pp/cm ³	[30]			
SMPS (L) + APS 3321	TSI	540 - 573	13-19,810 nm	[18]			
FMPS 3091 + APS 3321	TSI	500 - 560	5.6-20,000 nm	[4, 10, 11]			
EEPS 3090 + APS 3321	TSI	500 - 560	5.6-20,000 nm	[31]			
Wide R	ange Instrumer	ts for Particle	Sampling				
PWRAS	Naneum	60 and 250	2-20,000 nm	[5, 6, 31, 93]			
Wide Range Instruments for Real-time Measurements and Particle Sampling							
ELPI (+ Filter Stage)	Dekati	30	7-10,000 nm	[17]			
ELPI+	Dekati	17	6-10,000 nm	[94]			

Table 8: List of wide-range PSD instrumentation, measurement interfaces and studies where such systems have been used.

Table 9: Summary of real-time measurement methods for a physio-chemical analysis of particles or nano-objects in aerosol releases.

Release Meas.	Model	Range / Analysis	Ref
DPM	NIOSH 5040		[7, 19]
PAS	EchoChem	0 – 1000 fA	[6]

Table 10: Summary of measurement methods used to collect and characterise particles or nano-objects from aerosol releases.

Release Meas.	Model	Range / Analysis	Ref
ELPI	Dekati	30-10,000 nm	[7]
		Polycarb. mem./stage 2	[17]
ESP	NIOSH	TEM grid	[4, 6, 31]
	InTox Products	point-to-plane, TEM	[7]
	HCT 4650	point-to-plane, TEM	[28]
	Similar to TSI 3089	Cu TEM grid, TEM	[13]
	(Cheng: Uni Minnesota)	TEM grid, TEM	[30]
	Unspecified		[14]
Membrane	MCE		[4-6]
		15nm Pt coating, SEM; XPS, SIMS, AUC	[15]
		NIOSH 7402	[19, 27]
	SKC Button		[7]
	Polycarb., 50nm pore	Cu-TEM grid, TEM	[14]
	Polycarb., 400nm pore	SEM (Pt coating)	[18]
	PVC	gravimetric, ICP-AES	[27]
	Not specified	-	[23]
NAS	TSI 3089	TEM grid 2-100 nm	[17, 18]
PWRAS	Naneum, Nano-ID Select	2-20,000 nm	[5, 6, 31]
Release Container	NIST	balance, SEM/EDX	[24]
Surface Swab	ASTM D 7144-05a		[7]
TP	Fraunhofer		[4-6, 31]

APPENDIX B – MACHINING PROCESSES AND EMITTED PARTICLES

This appendix provides a summary of particles emitted by each machining process.

Table 11: Characterisation of release generated by machining of nano-composites.

Supplementary information provided by the authors is indicated by an attribute "+ suppl." next to the reference number.

Machining Process (Tool)	Particle Source (Nano-objects)	Sampler: Description of emissions	Study
Abrasion (sandpaper)	Composites: • PA+SiO ₂ NP (SiO ₂) • POM+CNT (CNT) • Cement+CNT (CNT) • Cement+CSH (CSH)	Cassette: SEM reveals powders generatedhave Ø of several μm (10-80μm). NP fromnano-composite can stick to particle surface.(Fig5d, CEM+CNT).AUC / laser diffraction : No loose nano-objects detected (in colloid suspension) .AUC: (Fig. 5f) CNT only as positive control• CNT only:7-100nm, peak at 30nm• POM only:>400nm• POM+CNT:>700nm• CEM+CNT:>130nmLaser diff: small amount of 2μm NP (all).	[15] + suppl.
Abrasion (Taber rotary)	Composites: • PA+SiO ₂ NP (SiO ₂) • POM+CNT (CNT) • Cement+CNT (CNT) • Cement+CSH (CSH)	SMPS: Most particles found below 200nm. Cassette: Insufficient material for physico- chemical investigation. Hypothesis that ultra-fine particles are emissions from driving motor (no proof).	[15] + suppl.
	Coatings: • PU+ZnO (ZnO) • Clearcoat+ZnO (ZnO) • Architectural coating (AC)+ZnO (ZnO)	SMPS: Indicates most particles >100nm: conclude that NPs remain embedded. Numbers detected are below statistical significance level. CPC: ZnO appears to reduce emissions from PU, but no effect on Clearcoat or AC. ESP: TEM reveal size of 20-100 nm ZnO NP and larger pigment particles (from AC).	[12]
	• Epoxy+CNT (CNT)	 SMPS+APS: Wide-range PSD made up of four modes: 326415nm; ≈680nm; ≈1200nm; 23002400nm. PC Membr.: Collection for SEM imaging. NAS: TEM imaging on C-backed TEM grids. Found matrix particles, CNT protruding and free-standing CNT. 	[18]
Abrasion (Taber linear)	• PET fabric + PVC coat + Nano-clay (Nano-clay)	SMPS: peak of Ø-modes• PET:80 nm• PET+PVC:80 nm• PET+PVC+ Nano-clay:50 nm	[16]
	Composites:	ELPI/stage2 -200nm polycarb. membrane:	[17]

Machining Process (Tool)	Particle Source (Nano-objects)	Sampler: Description of emissions	Study
	 PMMA+Cu NP (Cu) Polycarb+CNT (CNT) 	 SEM images of <u>PC-CNT</u>: NP found, but no CNT. NAS: TEM images of <u>PC-CNT</u>: no CNT found. <u>PMMA-Cu</u>: (Cu detected by EDX) abrasion: brush: Cu found in particles of µm Ø. SiC: Cu nearly detached from matrix. 	
Cutting (band-saw)	Composites: • [CF+CNT] in epoxy (CNT) • [Alumina fibres + CNT] in epoxy (CNT)	 FMPS+APS: found 4-5 modes. Abundance of 10-20 nm particles (spherical, agglomerated). ESP, TP: SEM and TEM show fibres of 30nm to 6µm Ø. Amongst fibres of 300nm Ø are several that are 10 µm long. 	[4]
Cutting (Wet, via diamond disc saw)	Composites: • [CF+CNT] in epoxy (CNT) • [Alumina fibres + CNT] in epoxy (CNT)	Emissions below detection.	[4]
	Composites: • Epoxy coated CNF (CNF) • CNF composite material (CNF)	 ELPI: results from PSD data: Ø 30 nm to 200 nm dominant. Ø>400nm from wet-saw cutting, Ø≈500nm from CNF. ESP: TEM from CNT bundle collected; no single CNT. 	[7]
	• Epoxy-CNF aerospace composite	 TEM (NIOSH 7402): Matrix fragments Free CNF CNF agglomerates & bundles EC (NIOSH 5040): Substantial amounts of nanoscale CNF. 	[19] + suppl.
Drilling (drill press)	Composites: • [CF+CNT] in epoxy (CNT) • [Alumina fibres + CNT] in epoxy (CNT)	 Cassette: SEM images found aggregates of respirable particles. ESP, TP: TEM images reveal CNT aggregates spherical <10nm fraction: is condensate from white smoke. All EM imaging shows HARN fibres, few with nano-scale dim. 	[6]
Drilling (hand held)	Bulk: Cement+SiO ₂ fumed (SiO ₂)	DiSC: Median of particle Ø 37-51 nm; range 19 -300 nm (as instrument).	[8]
FSW (<mark>plasma</mark>)	2 Aluminium alloys (None)	EEPS+APS (wide range): generation at High RPM: more dust mass / coarse pp. Low RPM: more ultrafine particles. Modes: 550nm from workpiece; 30nm Zn from lubricant. Incr. to 125nm by agglomeration.	[31]

Machining Process (Tool)	Particle Source (Nano-objects)	Sampler: Description of emissions	Study
		PWRAS/ICP-MS: large Zn fraction detected; only possible source is lubricant.	
Grinding (grinder)	• Epoxy-CNF aerospace composite	 TEM (NIOSH 7402): Matrix fragments Free CNF EC: (NIOSH 5040): Few nanoscale CNF. CPC-OPC: High concentrations of ultra-fine particles, but only few are CNF. 	[19] + suppl.
	 Granite Clay ceramic Hardwood (None) 	SMPS-APS: Data analysed by fitting two modes: ultra-fine: 9-10nm; oak ≈35nm coarse: 600 – 3,800 nm.	[30]
Grinding (not specified)	Silver colloid and NP (Ag NP)	SMPS: 2 modes appear at 20nm and 25nm Ø on opening grinder hatch. ESP: TEM images show agglomerates of 50- 60nm Ag NP.	[28]
Sanding (manual)	Composite: •CNT-enforced epoxy (CNT)	Cassette based sampler: TEM shows large particles of >300nm size with CNT protruding. No free CNT observed.	[14]
	• Epoxy-CNF composite / CNF Buckypaper laminate	TEM (NIOSH 7402): Shows evidence of CNF, regardless of ventilation conditions. EC: (NIOSH 5040): Few nanoscale CNF.	[19] + suppl.
Sanding (miniature sander)	Polyurethane (PU) or Architectural Coatings (AC): • PU-ZnO (ZnO) • AC-ZnO (ZnO) • AC-Fe ₂ O ₃ (Fe ₂ O ₃)	ESP: SEM images suggest mass loss is dominated by $\emptyset > 20 \mu m$. Abraded surface coating is source for coarse and fine particles (no abradant present)	[13]
Sanding (hand-held orbital Sander)	 PVA+TiO₂ (TiO₂) Acryl+CB (CB) Acryl+TiO₂ (TiO₂) Acryl+SiO₂ (SiO₂ sol) Coat+SiO₂ (SiO₂) 	FMPS / APS+Diluter: found 5 Ø-modes. Mode 3 (peak = 130-180nm) may indicate how ENP affect the dust size spectra.	[11] + suppl.
Sanding (belt sander)	• Epoxy-CNF aerospace composite	 TEM (NIOSH 7402): Matrix fragments No free CNF detected Clusters of spherical carbon particles EC: (NIOSH 5040): Few nanoscale CNF. 	[19] + suppl.

APPENDIX C – PARTICLE RELEASE MEASUREMENT AND CHARACTERISATION

Table 12: Summary of control measures, release measurement instrumentation and characterisation for machining processes and workpieces.

Meaning of codes: Column "St" (Structure): C = composite, NM = nano material; "Description of exposure": RT = real-time, SC = sample collection, PS = personal sampler, NC = number count, MC = mass concentration, DET = detection of existence, SA = surface area; II = inertial impactor, DC = diffusion cell.

Study	Machining Process	Particle Source	St	Nano- objects	Control Measures	PSD properties	Morphology from EM	Remarks
[4]	Wet-cutting (diamond saw)	Composites: • base-carbon • CNT-carbon • base-alumina • CNT-alumina	C / NM	CNT	 cutting wheel guard lubricant general ventilation 1 h⁻¹ RER PPE (N100 resp., gloves) 	165 nm (45–540 nm)	No data	Values with broken guard ; otherwise not distinguishable from background
	Dry-cutting (band saw)	All • base-carbon • CNT-carbon • base-alumina • CNT-alumina			 general ventilation 1 h⁻¹ RER PPE (N100 respirators, gloves) 	12, 230 nm 1000 nm 20 nm 20 nm 30 nm 25 nm	 Abundance of 10-20 nm particles (spherical, agglomerated) Fibres, 30nm - 6μm Ø, 300nm - several 10 μm long. Src: 1.6 to 3.8; BZ: 0.2 #/cm³. 	Fibre diameters: carbon: 6-7 μm alumina: 11 μm submicr: 5-20 nm
[5]	Solid-core drilling (drill press)	Composites: • base-alumina • CNT-alumina	C / NM	CNT	 general ventilation 1 h⁻¹ RER Lubricant PPE (N100 resp., gloves) 	No data	No data	
[6]	Solid-core	Composites:	C /	CNT	 general ventilation 1 	Srce: LS <hs></hs>		PSD: characterised at

Supplementary information provided by the authors is indicated by an attribute "+ suppl." next to the reference number. Refer also to the Glossary.

Study	Machining Process	Particle Source	St	Nano- objects	Control Measures	PSD properties	Morphology from EM	Remarks
	drilling (drill press)	All • base-carbon • CNT-carbon • base-alumina • CNT-alumina	NM		h ⁻¹ RER • Lubricant: water from spray bottle • PPE (N100 respirators, gloves)	<10 nm, 600-800 nm <40>nm <33>nm 30 / <50>nm 30 / <30>nm BZ: LS <hs> <60>nm <80>nm 30 / <80>nm 30 / <30>nm</hs>	Fibres/cm ³ 1.7 - 1.3 1.0 1.9 - 1.0 0.7	source (Srce) and breathing zone (BZ) for low and high drill speed (LS, HS); same sequence of composites. <10nm fraction is condensate from white smoke.
[7]	Wet-saw cutting of CNF composite	CNF composite material	C / NM	CNF	 Laboratory hood Single-pass ventil. + HEPA filter No dedicated extraction for wet-saw PPE 	ELPI: Ø 30-200nm dominant. Ø>400nm from wet- saw cutting	ESP: TEM from CNT bundle collected (Fig 2); no single CNT.	
	Chopping of epoxied CNF	Epoxy coated CNF	NM	CNF	Ventil. + HEPA filter PPE	Ø≈500nm CNF aggregated		
[8]	Manual drilling of concrete	Conventional concrete Emaco Nano- Crete R4 (BASF)	- C / NM	• Fumed silica (Evonik)	None reported (in the open air)	Median of particle Ø 37-51 nm; range 19 -300 nm (as instrument)	Not investigated	Higher emissions for Nano-Crete: intensity of drilling higher?
[10]	Sanding by hand-held orbital Sander	Painted plates: • 1 ref. paints (no NP) • 2 NP paints		• TiO ₂ (17 nm) • CB (95 nm)	• Stainless steel human exposure chamber w. HEPA filters: RER = 9.2 h^{-1} .	Ø-modes: Sander: 5 Release: 3 . NP affect pos. and conc. of rel. modes.	No details provided.	Particle back-ground <100 cm ⁻³ in chamber from HEPA filters: RER = 9.2 h ⁻¹ . Sander particles

Study	Machining Process	Particle Source	St	Nano- objects	Control Measures	PSD properties	Morphology from EM	Remarks
	(Metabo FSR 200 Intec)					No individual NP found.		collected in 0.03 m ⁻³ dust reservoir.
[11] + suppl.	Sanding by hand-held orbital Sander (Metabo FSR 200 Intec)	Painted plates: • 3 ref. paints (no NP) • 6 NP paints • 1 std. lacquer • 1 NP lacquer • 2 plates with filler cover		 3x TiO₂ forms: 1x Rutile, 2xAnatase Kaolinite CB Nano- SiO₂ sol Perlite 	• Stainless steel human exposure chamber w. HEPA filters: Vol = 20.6 m ³ ; RER = 9.2 h ⁻¹ .	• 5 Ø-modes: mode 3 (peak = 130- 180nm) may indicate if ENP affect dust size • 5 mat. groups: PVA, in/outdoor acryl, filler, coat	No details provided	Particle back-ground <100 cm ⁻³ in chamber from HEPA filters: RER = 9.2 h ⁻¹ . Sander particles collected in 0.03 m ⁻³ dust reservoir.
[12]	Abrasive Test (Taber)	Coatings: • Polyurethane (PU), 2-comp • Clearcoat (CUV) • Architectural Coating (AC) •Coat+ZnO	C / NM	 ZnO(1) 20-700nm ZnO(2) ZnO(3) 20-100nm; Pigment 200- 400nm 	Taber extraction of >2000L/min: replaced by 1500cc hood at 10.6 LPM air flow.	Distributions for ZnO nanoparticles provided only	Images of C1 by SEM (prepared by cryo-burst) and TEM show size of pigment and ZnO nanoparticles (see column "Nano-particles"). SMPS indicates most particles >100nm: conclude that NP remain embedded.	Taber extraction of >2000L/min: replaced by 1500cc hood at 10.6 LPM air flow. SMPS results were below min concentration, but values were still used to conclude the NP remain embedded.
[13]	Miniature Sander (Dremel 400 Series)	Coatings: Polyurethane (PU) Architectural Coating (AC), PU-ZnO AC-ZnO, AC-ZnO, AC-Fe ₂ O ₃ .	C / NM	• ZnO • Fe ₂ O ₃	Particle-proof enclosure	LAP / FMPS 1-18µm/100nm 5-17µm/100nm max ≈2µm 5-17µm <mark>5-17µm</mark>	Mass loss dominated by $\emptyset > 20 \mu m$. Abraded surface coating is source for coarse and fine particles (no abradant present)	Characterisation of ultra- fine particle fractions: FMPS, CPC, Photon cross-correlation. Coarse fractions: LAP, optical extinction counter.

Study	Machining Process	Particle Source	St	Nano- objects	Control Measures	PSD properties	Morphology from EM	Remarks
[14]	Manual sanding by operator	•CNT-enforced epoxy composite	C / NM	•CNT: Baytubes (Bayer) Ø= 10-50nm, length = 1-20 μm	 3 extraction options investigated: none / hood / class2 type A2 biosafety cab. (Baker: Sterilgard III 303) Monitoring Full-face respirator 6700 (3M 	tions he / be A2 Baker: b) rator		Poor performance of fume hood attributed to lack of front sash, rear baffles and low airflow. Biosafety cabinet was an effective control.
[15] + suppl.	Custom-built abrasive test	Composite plates, 4mm thick: • Polyamide + SiO ₂ nanofiller • Polyoxy- methylene (POM) + CNT nanofiller • Cement1 mortar + CNT nanofiller • Cement2 mortar + CSH nanofiller	C / NM	 SiO2 nanofiller Aerosil R8200 CNT Nanocyl NC7000 Calcium Silicate Hydrate (CSH) seed nano- particles 	Abrader enclosure, flushed with filtered air.	All: 2 modes •laser diff: 2 µm •SEM:10-80 µm Ultra-fines: -> •AUC (Fig. 5f): - Pos control - CNT:7-100nm max. = 30nm -POM:>400nm -POM+CNT: >700nm -CEM+CNT: >130nm	SEM reveals powders generated have Ø of several µm (2µm, 10- 80µm). NP from nano- composite can stick to particle surface (Fig5d, CEM+CNT). No loose nano-objects were found (detected as colloid by laser diffr. or AUC).	PSD by AUC: suspensions were pre- filtered using glass-fibre filter with 2.7µm cut-off.
	• Abrasive Test (Taber)	As above	C / NM	As above	No enclosure.	SMPS: More than 90% of all particles below 200nm Ø (Figure 3)	Collected samples too small for analysis	No explanation why size fraction is nearly entirely ultra-fine!
	Weathering	• PA	С/	As above	UV Chamber	No specific data	• No degradation of poly.,	CNTs are not easily

Study	Machining Process	Particle Source	St	Nano- objects	Control Measures	PSD properties	Morphology from EM	Remarks
	Test (Suntest XLS+)	 PA + SiO₂ POM POM + CNT Cement1 Cement1+CNT Cement2 Cement2+CSH 	NM				cracks. • Poly degrad. • > degrad w. CNT • No evidence of CNT on surface • CSH remains integrated	liberated by ultrasound (in liquid), but low doses were detected. Use Fe, B catalysts as CNT tracers.
[16]	Abrasive Test (Taber Linear Tester)	2 PVC coated PET fabrics rubbed against each other	C / NM	Nano-clay (IFTH, Lyon, France)	Enclosed flow cabinet with clean air from a H14 HEPA filter.	PET,PET+PVC Ø- mode: 80 nm Nano-clay: Ø-mode: 50 nm		Method verified: 20nm SiO_2 , 40 / 60 / 100nm PSL on cotton fabric.
[17]	Abrasive Test (Taber Linear Tester)	PMMA + 10% Cu NP: (PMMA-Cu) Polycarb. + 3% CNT: (PC-CNT)	C / NM	• Cu NP • CNT	Sealed HEPA filtered glove box, 150 LPM air flow rate.	SiC paper: P1200: large no of ultrafine # P120: fewer # and coarser.	SEM of 200nm PC from ELPI/stage2: <u>PC-CNT</u> : NP found, no CNT. TEM: from NAS: <u>PC-CNT</u> : no CNT <u>PMMA-Cu</u> : Cu detected by EDX; <i>brush</i> : Cu in µm particles. <i>SiC</i> : Cu nearly detached.	
[18]	Abrasive Test (Taber)	Epoxy + CNT (0, 0.1, 1 wt.%)	C / NM	CNT	Enclosure chamber surrounding abrasion wheel.	Four modes found in each case (Table 1). CNT cause 70nm->90nm shift in mode1.	Only few particles from abr. wheel (EDX). Matrix particles, CNT protruding, free individual CNT (!)	Authors indicate that TEM images prove free- standing CNT are released.
[19] + suppl.	Wet saw cutting using diamond	CNF-Composite	C / NM	CNF	Without controls Inside ventilated	Substantial amounts of nanoscale CNF	 Matrix fragments Free CNF CNF agglomerates & 	CNF quantified by elemental carbon (EC) reading and identified by

Study	Machining Process	Particle Source	St	Nano- objects	Control Measures	PSD properties	Morphology from EM	Remarks
	blade table booth saw		(from EC) and 300-10,000nm	bundles	TEM of collected particles.			
	Dry surface grinding	CNF-Composite	C / NM	CNF	LEV: Measurement at edge of LEV inlet.	Nanoscale and 300-10,000nm	Matrix fragments Free CNF	High concentration of ultra-fine particles, only few CNF.
	Tabletop belt sanding	Tabletop belt sanding CNF-Composite C / NM CNF LEV: Measurement at edge of LEV inlet.		LEV: Measurement at edge of LEV inlet.	atNo nanoscale, but 300-10,000nm present• Matrix fragments • Clusters of spherical carbon particlesCNF no with LET		CNF not detected in BZ with LEV operational	
	Hand sanding inside spray booth	CNF-Composite and CNF Buckypaper laminate	C / NM	CNF	Vent on Vent off	No nanoscale, but 300-10,000nm present	Matrix fragments Free CNF	TEM shows evidence of CNF, regardless of ventilation conditions.
[24]	None (weathering)	Silica NP in epoxy (EPON 828)	C / NM	SiO ₂ NP	Enclosure	N/A	SEM/EDX: particles detected and identified.	Exposure in SPHERE UV chamber (NIST)
	None (weathering)	MWCNT in epoxy	C / NM	MWCNT	Enclosure	N/A	SEM/EDX: no CNT detected in release container	Exposure in SPHERE UV chamber
[25]	Weathering + fanning + abrasion)	TiO ₂ photo- catalyst paint (Allstar, Taiwan)	C / NM	TiO ₂ NP	Enclosure	Fig5: mode peak initially at 55nm; moves to ≈125nm w time.	Not investigated	Wear processes: • UV exposure • fan blower • rubber knife
[27]	Milling	Li-titanate metal oxide (Li-Ti MO)	NM	Li-Ti-MO	-		Data for Wet Mill (Table I), using PVC membrane: 0.026 mg/m ³	Use CPC and OPC in combination.

Study	Machining Process	Particle Source	St	Nano- objects	Control Measures	PSD properties	Morphology from EM	Remarks
[28]	Grinding	Silver colloid and NP	NM	Ag NP	Vent hood above grinder, local air- conditioner Opening grinder hatch: 2 modes appear at 20nm and 25nm Ø.			
[30]	Grinder (Dremel Multipro 395)	 Granite Clay ceramic Oak hardwood 	(C)	None	Stainless-steel chamber, HEPA- filtered air (air cleaner ACE mod 73-800G) SMPS-APS data analysed by fitting two modes: ultra-fine : 9-10nm; oak ≈35nm coarse : 0.6–3.8 µm		TEM images of mostly coarse particles.	
[31]	FSW	Aluminium alloys: • 6061-T6 • 5083-H111	(C)	None	Snorkel fume extractors (LEV): Turned off during exp.	High RPM gen. more dust mass / coarse pp. Low RPM gen. more ultrafines. Fewer pp at BZ than source	Modes: 550nm from workpiece; 30nm Zn from lubricant. Increase to 125nm by agglomeration; Confirmed by EDX and PWRAS / ICP-MS.	Sampl. locations: TP: at BZ ESP: at source PWRAS: near BZ
[32]	Orthogonal Milling	KC725M grade insert (carbide + Al-TiN coating)	NM	Al-TiN coating (by PVD)	Milling process is inside a G-Class Plexiglas box	lilling process is Iside a G-Class lexiglas box Iexiglas box Iexigla		

APPENDIX D – PARTICLE AND NANO-OBJECT RELEASE DATA

Table 13: List of release measurements (total particle number conc). instrumentation and characterisation conducted in pertinent studies.

Meaning of codes: Real-time data (all): values in between $\uparrow_{}$ represent peak values, BD = below detection; BSS = below statistical significance; T/O/EC= Total Carbon TC / Organic Carbon OC / Elemental Carbon EC, SA = surface area; "Remarks": BZ = breathing zone, TPNC = total particle number count.

Study	Machining Process	Particle Source	FMPS SMPS ELPI, EEPS (10 ⁶ cm ⁻³)	APS LAP <u>ELPI</u> (cm ⁻³)	CPC DiSC <u>Tot. NC</u> (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (µm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
[4]	-	background	≈0.005	11.4 ↑15¦	3 – 4	0.013	<0>	1.3•10 ³	
	Dry-cutting	base-carbon	0.319 ↑0.7¦ 0.283 ↑ <mark>>5</mark> ¦	777.5 1003.8 ↑2400¦	>200-300	5.41 5.61	- <3.8>	313 •10 ³ 457 •10 ³	24-ply, Loc1 (BZ) 24-ply, Loc 2
		CNT-carbon	0.153 ↑7¦ 0.294 ↑ <mark>>5</mark> ¦	215.7 867.1 ↑2400¦	>200-300	2.40 8.38	-	116 •10 ³ 393 •10 ³	24-ply, Loc1 (BZ) 24-ply, Loc 2
		base-alumina	0.088 0.148 ↑≈0.2¦	72.2 135.2↑300¦	100-200	0.73 1.19	2.0 <0.2> <1.6>	32 •10 ³ 77 •10 ³	4-ply, Loc 1 (BZ) 4-ply, Loc 2
		CNT-alumina	0.028 0.038 ↑0.05¦	62.2 285.3↑600¦	10-30 (1-ply)	0.80 2.11	- <1.6>	45•10 ³ 235•10 ³	4-ply, Loc 1 (BZ) 4-ply, Loc 2
	Wet-cutting	all	>0.009-0.012	-	-	0.02-0.04	-	-	guard OK

Supplementary information provided by the authors is indicated by an attribute "+ suppl." next to the reference number. Refer also to the Glossary.

Study	Machining Process	Particle Source	FMPS SMPS <u>ELPI</u> , <u>EEPS</u> (10 ⁶ cm ⁻³)	APS LAP ELPI (cm ⁻³)	CPC DiSC Tot. NC (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (µm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
		all	0.014 ↑0.015¦	-	-	-	-	-	guard OK, reduced lubricant flow
		base-carbon	0.094 ↑0.55¦	47.6 ↑381¦	-	0.054	-	116•10 ³	broken guard
[5]	-	background	0.018-0.020	-	-	-	-	-	Figs 5A,B
	Solid-core drilling,	base-alumina	0.03-0.05 < ≈0.70> 0.05-1.30	-	-	-	-	-	725 RPM, 1-ply <2-ply> 1355 RPM, 1-ply
	1/4" drill bit	CNT-alumina	< 0.1-0.4> <0.2-1.0>	-	-	-	-	-	725 RPM, <2-ply> 1355 RPM, <2-ply>
	Solid-core drilling,	base-alumina	0.020-0.025 < ≈0.30>	-	-	-	-	-	725 RPM, 1-ply <2-ply>
	3/8" drill bit		0.05-1.00 < ≈3.00>	-	-	-	-		1355 RPM, 1-ply <2-ply>
		CNT-alumina	≈0.02 <0.07-3.00> 0.02-0.70 <0.05-7.00>	-	-	-	-	-	725 RPM, 1-ply <2-ply> 1355 RPM, 1-ply <2-ply>
[6]	-	background	0.0042	12 ↑137¦	-	-	<0>	9 ↑20¦	Source & BZ
	Solid-core drilling,	base-alumina	0.0500 ↑3.600¦ 0.0190 ↑0.450¦	31 <mark>↑</mark> 3877¦ 30 ↑433¦	-	-	-	13 <u>↑</u> 86¦	725 RPM, 3-ply @BZ

Study	Machining Process	Particle Source	FMPS SMPS ELPI, EEPS (10 ⁶ cm ⁻³)	APS LAP ELPI (cm ⁻³)	CPC DiSC Tot. NC (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (µm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
	3/8" drill bit		0.1600 ↑10.000¦ 0.0160 ↑0.790¦ 0.0068 ↑0.150¦	128			<1.3> <1.0>	25 <u>↑</u> 666¦	1355 RPM, 3-ply @BZ Wet drilling, 3-ply
		CNT-alumina	0.0850 ↑3.900 0.0430 ↑2.900 0.1800 ↑11.000 0.0460 ↑1.300 0.0087 ↑0.200	12 ↑ <mark>1746</mark> 30 ↑666 96 ↑5849 59 ↑5155 13 ↑136	-	-	<1.0> <0.7>	23 ↑425¦ 51 ↑686¦	725 RPM, 3-ply @BZ 1355 RPM, 3-ply @BZ Wet drilling, 3-ply
		base-carbon	0.1300	206	-	-	<1.7> <1.9>	-	1355 RPM, 22-ply @BZ
		CNT-carbon	0.0840	155 ↑548¦ 178 ↑1100¦	-	-	-	-	1355 RPM, 22-ply @BZ
[7]	-	background (TC)	-	-	<mark>≈10</mark> 26-29	0.012-0.016 0.033-0.040 <u>0.017</u> <u>0.000,57</u>	-	-	PM ₁₀ (Indoor) PM ₁₀ (Outdoor) TC Inhalable (Tab I) TC Surfaces (TabII)
	Chopping of epoxied CNF	Epoxy coated CNF	-	-	<mark>≈11</mark>	<mark>≈0.010</mark> <u>0.221</u>	-	-	<mark>PM₁₀</mark> TC Inhalable (Tab I)
	Wet-saw cutting of CNF comp.	CNF composite material	-	-	<mark>12-17</mark>	0.040-0.161 <u>1.094</u> 0.003,68	-	-	PM ₁₀ TC Inhalable (Tab I) TC Surfaces (TabII)

Study	Machining Process	Particle Source	FMPS SMPS ELPI, EEPS (10 ⁶ cm ⁻³)	APS LAP ELPI (cm ⁻³)	CPC DiSC Tot. NC (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (µm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
[8]		background	-	-	7.605	-	-	-	At distance
		ldle-running drill	-	-	39.033 195.616	-	-	-	Up-wind Down-wind
	Manual drilling	Conventional concrete	-	-	15.960 <mark>22.889</mark>	-	-	-	Up-wind Down-wind
	Manual drilling	Emaco Nano- Crete R4 (BASF)	-	-	29.545 70.981	-	-	-	Up-wind Down-wind
[10]	ventilation	background	> 0.000,01	-	-	-	-	-	
	Sanding by hand-held	Sander properties	0.1180, 0.1850, 0.0007	141 89	<u>303.9</u>	-	-	-	Modes = <mark>9.8</mark> , 16, <mark>179</mark> , 904, 1320 nm
	orbital sander	Ref. paint	<mark>0.0181</mark>	2257 482	<u>20.8</u>	-	-	-	Modes = <mark>140</mark> , 1020, 2020 nm; <mark>Prod Em.</mark>
	(Metabo FSR 200 Intec)	NP Paint 1	<mark>0.0103</mark>	3005 1182	<u>14.5</u>	-	-	-	Modes = <mark>152</mark> , 1020, 1840 nm; <mark>Prod Em.</mark>
		NP Paint 2	0.0238	3194 599	27.6	-	-	-	Modes = <mark>144</mark> , 1020, 2160 nm; <mark>Prod Em.</mark>
[11] +	ventilation	background	> 0.000,2	(diluted)	-	-	-	-	
suppl.	Sanding by	Polyvinyl-	0.294	46,600	<u>341</u>	-	-	-	G1R: Prod Emiss.

Study	Machining Process	Particle Source	FMPS SMPS ELPI, EEPS (10 ⁶ cm ⁻³)	APS LAP <u>ELPI</u> (cm ⁻³)	CPC DiSC <u>Tot. NC</u> (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (μm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
	hand-held	acetate (PVA)	0.260	751	<u>80</u>				Sanding / Sander
	orbital Sander	PVA + TiO ₂ (9.8%)	0.356 <mark>0.285</mark>	19,300 <mark>317</mark>	<u>375</u> 90	-	-	-	G1A - (220nm) Sanding / <mark>Sander</mark>
	(Metabo FSR 200 Intec)	PVA + TiO ₂ (10.0%)	0.599 <mark>0.317</mark>	134,000 <mark>117</mark>	<u>733</u> 416	-	-	-	G1B – (<100nm) Sanding / <mark>Sander</mark>
		PVA + Kaolin. (14.7%)	0.459 <mark>0.292</mark>	63,000 <mark>448</mark>	<u>522</u> 230	-	-	-	G1C – (200nm) Sanding / <mark>Sander</mark>
		Acryl	0.351 <mark>0.241</mark>	4,000 <mark>148</mark>	<u>355</u> 114	-	-	-	G2R: Prod Emiss. Sanding / Sander
		Acryl+CB (2.5%)	0.332 <mark>0.155</mark>	6,700 <mark>201</mark>	<u>339</u> <u>118</u>	-	-	-	G2A – (95nm) Sanding / <mark>Sander</mark>
		Acryl + TiO ₂ (10.0%)	0.406 <mark>0.318</mark>	5,600 <mark>895</mark>	<u>411</u> <u>93</u>	-	-	-	G2B – (17nm) Sanding / <mark>Sander</mark>
		Outdoor Acryl	0.395 <mark>0.298</mark>	4,900 231	<u>400</u> <u>102</u>	-	-	-	G3R: <u>Prod Emiss</u> . Sanding / <mark>Sander</mark>
		Acryl + SiO₂ (≈10%)	0.340 0.232	6,900 <mark>190</mark>	<u>347</u> 145	-	-	-	G3A – (7nm) Sanding / <mark>Sander</mark>
		CaCO ₃ filler	0.564 <mark>0.295</mark>	59,900 <mark>95</mark>	<u>624</u> 329	-	-	-	G4R: Prod Emiss. Sanding / Sander

Study	Machining Process	Particle Source	FMPS SMPS ELPI, EEPS (10 ⁶ cm ⁻³)	APS LAP ELPI (cm ⁻³)	CPC DiSC Tot. NC (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (µm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
		CaCO ₃ + perlite	0.719 <mark>0.336</mark>	16,900 <mark>102</mark>	<u>736</u> 400	-	-	-	G4A Sanding / <mark>Sander</mark>
		UV hard coat	2.420 0.271	52,400 <mark>157</mark>	<u>2470</u> 2200	-	-	-	G5R: Prod Emiss. Sanding / Sander
		Coat + SiO ₂ (5%)	0.644 <mark>0.279</mark>	9,900 <mark>706</mark>	<u>654</u> 374	-	-	-	G5A – (<50nm) Sanding / <mark>Sander</mark>
[12]	-	Background	BSS (<4E-6)	-	0.000,03	-	-	-	
	Abrasive Test (Taber)	Polyurethane (PU), 2-comp	BSS	-	<mark>1.17</mark> 0.23	-	-	-	A1 (fibre board) / A3 (steel plate)
		PU-ZnO	BSS	-	0.03, 0.07	-	-	-	A2, A4 (see above)
		Clearcoat, Desmolux U100 (CUV)	BSS	-	0.45	-	-	-	B1 (UV curable)
		CUV-ZnO	BSS	-	0.40	-	-	-	B2
		Architectural Coating (AC)	BSS	-	0.08	-	-	-	C1
		AC-ZnO	BSS	-	0.10	-	-	-	C2
[13]		background	-	-	≈0.000,01	-	-	-	0.2 #/cc in 300cc

Study	Machining Process	Particle Source	FMPS SMPS ELPI, EEPS (10 ⁶ cm ⁻³)	APS LAP ELPI (cm ⁻³)	CPC DiSC Tot. NC (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (µm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
	Miniature Sander	Polyurethane (PU), 2-comp	0.2 (Ø<100nm: .12)	-	<mark>1,200</mark> (diluted)	-	-	-	3.5E8 #/cc in 0.3L 2.0E8 #/cc in 10L
	(Dremel 400 Series)	PU-ZnO	0.22 (Ø<100nm: .15)	-	<mark>1,800</mark> (diluted)	-	-	-	5.5E8 #/cc in 0.3L 2.2E8 #/cc in 10L
		Architectural Coating (AC)	<mark>0.16</mark> (Ø<100nm: .15)	-	<mark>≈15</mark>	-	-	-	<mark>≈.05E8 #/cc in 0.3L</mark> 1.6E8 #/cc in 10L
		AC-ZnO	0.205	-	<mark>≈30</mark>	-	-	-	<mark>≈0.1E8 #/cc in 0.3L</mark> 2.05E8 #/cc in 10L
		AC-Fe ₂ O ₃	0.205	-	<mark>≈30</mark>	-	-	-	<mark>≈0.1E8 #/cc in 0.3L</mark> 2.05E8 #/cc in 10L
		Overall	-	-	0.6-63.6	-	-	-	Room 10m ² x 3m
[14]	-	background	-	-	- 3.728- 3.739 <mark>0.000,03</mark>	0.000,02 0.000,45 0.000,01	-	-	glovebox, no act. Room (closed) Biosaftey cabinet
	Manual sanding by operator	CNT-enforced epoxy composite	-	-	3.889 3.765 <mark>1.742</mark> 0.000,06 ↑0.008,00¦	0.002,68 0.010,60 0.031,50 0.000,03	-	-	Near source: • glovebox • ambient, no extr. • Fume hood • Biosafety Cab.

Study	Machining Process	Particle Source	FMPS SMPS ELPI, EEPS (10 ⁶ cm ⁻³)	APS LAP ELPI (cm ⁻³)	CPC DiSC Tot. NC (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (µm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
			-	-	3.889 <mark>1.989</mark> 1.350	0.002,68 <mark>0.021,40</mark> 0.000,20	-	-	Breathing Zone BZ: • ambient, no extr. • Fume hood • Biosafety Cab.
[15] + suppl.	-	background	0.0020 0.0015-0.0040	-	-	-	-	-	Custom-built test Taber Abraser
	Custom-built abrasive Test	• PA • PA + SiO_2 • POM • POM + CNT • Cement1 • Cement1 + CNT • Cement2 • Cement2 + CSH	0.0005 0.0050-0.0650 0.0004-0.1000 0.0004 BD BD BD BD	-	-	-	-	-	 Set up encapsulated Data from Table1 Results from cements dominated by sanding paper debris (0.01- 1.00).
	Abrasive Test (Taber Abraser 352G)	• PA • PA + SiO_2 • POM • POM + CNT • Cement1 • Cement1 + CNT • Cement2	0.0037 0.0047 0.0055 0.0058 0.0100 0.0039 0.0090	-	-	-	-	-	 Set up not encapsulated Data from Table1
Study	Machining Process	Particle Source	FMPS SMPS <u>ELPI</u> , <u>EEPS</u> (10 ⁶ cm ⁻³)	APS LAP ELPI (cm ⁻³)	CPC DiSC <u>Tot. NC</u> (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (µm ² • cm ⁻³)	Remarks
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			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
		• Cement2 + CSH	0.0067						
	•Weathering Test (Suntest XLS+)	• POM • POM + CNT	-	-	-	-	-	-	CNT release rate ≈10 µg cm ⁻² year ⁻¹ (from SIMS)
[16]	ventilation	background	0.005 E-6	-		-	-	-	@ 6nm: <5#/4min
[17]	ventilation	background	-	< 10	-	-	-	-	In glove box
	Abrasive Test (Taber Linear Tester)	Polycarb. + CNT (3%)	<u>370 E-6</u> <u>200 E-6</u> <u>180 E-6</u> <u>50 E-6</u> <u>240/535 E-6</u> <u>1800/3,565 E-6</u>	<u>70</u> <u>225</u>	-	-	-	-	Bin max. / TPNC steel brush,60RPM red. speed: 40RPM 30 RPM 15RPM incr. force: 1.2 kg 2.1 kg
		PMMA + Cu NP(10%)	<mark>10,200</mark> / 12,500 E-6 <mark>460</mark> / 848 E-6	<u>10</u> 70	-	-	-	-	Bin max. / TPNC P1200 SiC paper P120 SiC paper
[18]		background	0.0025 – 0.0035	≈10	-	-	-	-	
	Abrasive Test (Taber	Epoxy + CNT	0.008 - 0.020	1000-3000	-	-	-	-	

Study	Machining Process	Particle Source	FMPS SMPS <u>ELPI</u> , <u>EEPS</u> (10 ⁶ cm ⁻³)	APS LAP ELPI (cm ⁻³)	CPC DISC <u>Tot. NC</u> (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM SMPS/OPC (µm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
	Model 5135)								
[19] + suppl.	Wet saw cutting,	CNF- Composite	-	-	(20-300nm)	5.75 <u>0.39</u>	-	-	Process area
	no controis				1.934	<u>1.00</u>			 BZ (Breathing Zone)
	Wet saw cutting inside ventilated booth	CNF- Composite	-	-	2.605	<u>1.9</u> <u>0.48</u> 1.13 <u>0.91</u>	-	-	 Process area inside booth Outside booth BZ
	Surface grinding with LEV	CNF- Composite	-	-	491.599 42.088	0.9 <u>0.045</u> 0.5 <u>0.014</u>	-	-	 Process area at edge of LEV inlet BZ
	Belt sanding with LEV	CNF- Composite	-	-	0 - 0	18.5 <u>0.076</u> <u>0.008</u>	-	-	 Process area at edge of LEV inlet BZ
	Hand sanding inside venti- lated booth	CNF- Composite and CNF Buckypaper	-	-	0	3.09 <u>0.079</u> <u>ND</u>	-	-	Vent off: • Process area • BZ

Study	Machining Process	Particle Source	FMPS SMPS <u>ELPI</u> , <u>EEPS</u> (10 ⁶ cm ⁻³)	APS LAP <u>ELPI</u> (cm ⁻³)	CPC DiSC Tot. NC (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (µm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
		laminate	-	-	(20-300nm) 0	0.16 <u>0.011</u> <u>0.007</u>	-	-	Vent on: • Process area • BZ
[25]	-	background	< 0.000,020	-	-	-	-	-	simulation box
	Weathering + fanning + abrasion	TiO ₂ photo- catalyst paint (Allstar, Taiwan)	0.000,012 0.000,449 0.000,442 0.000,525 0.000,629	-	-	-	-	-	simul. time, (mode): 2 min (36.5nm) 30 min (107.3nm) 60 min (127.1nm) 90 min (127.7nm) 120 min (119.6nm)
[27]		background	-	-			<0.000,020	-	
	Milling	Li-titanate metal oxide (Li-Ti MO)	-	-	-	-	0.026	-	
[28]		background	0.040 - 0.088 0.026	-	-	-	-	-	Ø-range 10-200 nm vent operating
	Grinding	Silver colloid and NP	0.075	-	-	-	-	-	opening grinder: modes at 20+25nm
[30]	ventilation	background	-	-	0.05	-	-	-	-

Study	Machining Process	Particle Source	FMPS SMPS ELPI, EEPS (10 ⁶ cm ⁻³)	APS LAP ELPI (cm ⁻³)	CPC DiSC <u>Tot. NC</u> (10 ³ cm ⁻³)	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (µm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
	Grinder (Dremel Multipro 395)	 None Granite Clay ceramic Oak hardwood 	0.0065 0.0100 0.0500 0.8000	3 19 400 12	-	-	-	-	SMPS: Ultrafine mode APS: Coarse mode
[31]	-	background	<u> ↑0.0081¦ 0.0021</u>	↑53¦ 20	<u></u> 18.4¦ 2.8	0.007	-	12.2	avg. over 3days
	FSW	Al-alloy: 6061-T6	<u>↑3.900¦ 0.0300</u> <u>↑2.800¦ 0.0350</u>	↑739¦ 25 ↑1019¦ 20	↑ >500¦ 46.0 ↑ >500¦ 13.0	↑2.09¦ 0.029 ↑0.28¦ 0.018	-	239.0 195.0	Source: 1A: 1500 RPM 1B: 900 RPM
			<u>↑0.250¦ 0.0041</u> <u>↑0.160¦ 0.0057</u>	↑17¦ 8 ↑26¦ 11	↑150¦ 4.6 ↑42¦ 5.1	↑1.74¦ 0.022 ↑0.81¦ 0.015	0.0132	14.8 19.2	BZ: 1A: 1500 RPM 1B: 900 RPM
		Al-alloy: 5083-H111	<u>13.000¦ 0.0210</u> <u>12.600¦ 0.0290</u>	↑3055¦ 59 ↑2309¦ 30	↑>500¦ 72.0 ↑>500¦ 11.0	↑1.74¦ 0.022 ↑0.81¦ 0.015	-	138.0 191.0	Source: 2A: 1500 RPM 2B: 900 RPM
			<u>↑0.200¦ 0.0053</u> <u>↑0.048¦ 0.0048</u>	↑282¦ 35 ↑31¦ 15	↑25¦ 2.5 ↑130¦ 4.0	↑1.74¦ 0.022 ↑0.81¦ 0.015	0.0279	20.6 18.0	BZ: 2A: 1500 RPM 2B: 900 RPM
[32]	Orthogonal Milling	KC725M grade insert: (carbide+Al-	390-820-270- 370 420-810-800-	20,300 / 2,300 11,400 /	-	-	-	-	SMPS: Ø=10-20-100- 250-736 nm: APS:

Study	Machining Process	Particle Source	FMPS SMPS ELPI, EEPS (10 ⁶ cm ⁻³)	APS LAP ELPI (cm ⁻³)	CPC DISC <u>Tot. NC</u> (10^{3} cm^{-3})	DustTrak OPC-RPM <u>T/O/EC</u> (mg• m ⁻³)	7400PCM 7402 TEM <fib.cm<sup>-3> (mg• m⁻³)</fib.cm<sup>	DC (SA) NSAM <u>SMPS/OPC</u> (µm ² • cm ⁻³)	Remarks
			0.5 (@10nm) 5 (@100nm)	10,000 100,000	(3007) 100 1000	100 100	N/A	TB: 2,500 A: 10,000	Upper Operation Limit
		TiN coating)	300 430-830-290- 350 430-790-860- 310	7,100 14,500 / 100 2,500 / 2,000 <22,500> / <3,200> <13,000> / <8,300> <17,900>/ <400> <4,600> / <2,700>					Ø=0.5-1 / 1-10µm: wet / dry, Speed = 5 ,15 m/s, feed =0.125 <0.2>

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